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NEWS OF ENVIRONMENTAL RESEARCH IN CINCINNATI, MAY-DECEMBER 1973

National Environmental Research Center
Cincinnati, Ohio

April 1974

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A series of reports on the following subjects: consumerism and solid wastes; constraints to spreading sewage sludge on cropland; CAM-1: using enzymes to detect insecticides; plastics and incineration; using porous pavement to control runoff; relating socio-economic variables to technology for environmental management; oil identification: state of the art; the EPA-DC pilot plant for water pollution control; monitoring radionuclides in reactor effluents; using reclaimed rubber tires in road dressings; conserving water at home; removing organic matter from drinking water; and catalytic converters used in health effects studies.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

As part of these activities, each of the laboratories of NERC-Cincinnati outlines various research problems of their concern and elaborate on how they are being handled. Topics of interest have included research concerning advanced waste treatment, industrial waste treatment, solid and hazardous waste, water supply research, methods development and quality assurance research, and environmental toxicology research.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

CONTENTS

Consumerism and Solid Wastes 1
Richard H. Ongerth and Henry Johnson

Constraints to Spreading Sewage Sludge on Cropland . . . 7
G. K. Dotson

CAM-1: Using Enzymes to Detect Insecticides 11
John E. Brugger

Plastics and Incineration 15
Robert C. Thurnau and Nancy S. Ulmer

Using Porous Pavement to Control Runoff 21
Hugh Masters

Relating Socio-Economic Variables to Technology for Environmental Management 25
Robert M. Clark and Haynes C. Goddard

Oil Identification: State of the Art 29
F. K. Kawahara and E. C. Julian

The EPA-DC Pilot Plant for Water Pollution Control . . . 33
D. F. Bishop and J. M. Smith

Monitoring Radionuclides in Reactor Effluents 39
Herman L. Krieger and Bernd Kahn

Using Reclaimed Rubber Tires in Road Dressings 43
Richard A. Carnes

Conserving Water at Home 47
Harry E. Bostian

Removing Organic Matter from Drinking Water; Monitoring Treatment Processes 51
J. Keith Carswell, Ralph W. Buelow, and James M. Symons

Catalytic Converters Used in Health Effects Studies . . 55
J. K. Burkart, W. Moore, R. C. Hinners, and J. F. Stara

News of Environmental Research in Cincinnati

SOLID WASTE RESEARCH

U.S. Environmental Protection Agency

ANOTHER NEWSLETTER?

Yes! This pertinent fact sheet reports the environmental research being conducted at the U.S. Environmental Protection Agency's National Environmental Research Center in Cincinnati.

The effects of environmental science and technology are being announced in many ways—through reports, articles, bulletins, newsletters. In separate issues of this fact sheet, each of the Laboratories of the Cincinnati Center will outline various research problems of their concern and elaborate on how they are being handled. Topics of interest will be supplied by Advanced Waste Treatment Research Laboratory, Analytical Quality Control Laboratory, Edison Water Quality Research Laboratory, Environmental Toxicology Research Laboratory, Radiochemistry & Nuclear Engineering Research Laboratory, Solid Waste Research Laboratory and Water Supply Research Laboratory.

Copies of News of Environmental Research in Cincinnati *are available from the Technical Information Office, National Environmental Research Center, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.*

Andrew W. Breidenbach, Ph.D.
Director
National Environmental Research Center
Cincinnati

CONSUMERISM AND SOLID WASTES

Richard H. Ongerth and Henry Johnson

Almost everyone generates some trash. The most recent estimate for the United States is 6 lb/person/day. But generating wastes is not the only way the general public influences solid waste management; frequently they must approve financing improvements or alterations of waste handling and disposal systems. The public is often called upon to participate in public hearings of a planning commission. Naturally, any system requiring consumer participation, such as recycling, requires active public approval. Even where direct public judgment is not sought or called for, adverse public opinion or protest can force the alteration of well-engineered plans.

An increasing awareness of the importance of public attitudes is reflected in the scope and results of three contracts (see page 6) monitored by the Cincinnati National Environmental Research Center, Solid Waste Research Laboratory (NERC–SWRL).

All three deal with the interaction between the general public, or some specific segment of it, and waste disposal systems. All three have considerably expanded our understanding of the importance of public opinion in solid waste

management. But before discussing some of the significant results of these contracts, let's consider when and how attitudinal research would prove a useful tool in waste management.

Need for Attitudinal Research

Planning grant files of the U.S. Environmental Protection Agency contain many examples of waste management plans that had to be altered or scrapped because of public controversy. In a contract A Study of Public Attitudes and Problems of Solid Waste Disposal (General Behavioral Systems, Torrance, Calif.), the solid waste management efforts of 10 cities are described. Notable are the efforts in Sioux City, Iowa, and San Francisco, California, where, between 1968 and 1970, consumer pressures were instrumental in forcing alteration of technically and economically feasible plans.

In fact over the past 10 years, most major cities in the country have been faced with a situation where the public has had the power of approval or rejection over carefully engineered and managed solid waste handling and disposal alternatives. Another EPA study (Sheaffer, Jr. R., et al., Decision Making and Solid Waste Disposal, Research Grant No. EP-00281, U.S. Environmental Protection Agency, Research and Monitoring Division, 1971) of 20 proposed sanitary landfills showed that controversy played a major role in whether or not the proposal was successful (Table 1). To paraphrase the author of that research study, it is only natural for a planning commission after listening to 350 irate citizens opposing one plan at a public hearing to rule in favor of an unopposed plan.

TABLE 1. EFFECTS OF CONTROVERSY ON 20 PROPOSED LANDFILLS

Proposals	Protested	Uncontested
Successful	7	5
Unsuccessful	8	0

There are on record cases involving disposal other than municipal wastes where public attitudes have forced changes or abandonment of plans. Many of these have received broad national news coverage as an indication of their importance. One was when the Atomic Energy Commission planned to dispose of solidified high-level radioactive wastes, a by-product of the nuclear power industry. The AEC, as the result of spending $7 to $8 million in feasibility studies and site preparation, planned to bury the wastes in bedded salt deposits near Lyons, Kansas. Public controversy, spearheaded by The Sierra Club, was cited as the reason the State of Kansas blocked plans and announced at least temporary abandonment by the AEC of the Lyons disposal site plans (Solid Waste Report, 3(11): 104, May 29, 1972, Business Publishers, Inc., Silver Springs, Md.).

Another case involved disposal of the chemical 2,4,5-T, commonly known as herbicide orange. According to a draft report by TRW (Vol. 14, Contract #68-03-0089, Recommended Methods for Disposal of Hazardous Materials), the Air Force has 8.2 million pounds of this material to dispose of. As a result of technical feasibility studies, incinerators of Monsanto Corporation at St. Louis, Missouri, and Rollins Purle Incorporated, Houston, Texas, had been selected for incinerating this material, which was formerly used as a defoliant in Viet Nam but banned because of its teratogenicity. Public controversy has subsequently squelched the above incineration plans.

Perhaps the best known case is that of the Army's plans to transport 130,000 pounds of GB nerve gas across seven southern states for final disposal at sea. Although the Army eventually went through with the plans, public controversy seriously delayed the shipment plans and kept the story on the front pages of the Nation's newspapers for nearly a month. In the end (August 20, 1970), the Pentagon released a statement that henceforth obsolete nerve gas would be incinerated at its point of storage (Facts on File, Inc., 119 W. 57th St., New York, N.Y. 10019).

One common factor in these cases is the role of public dissent in disrupting carefully developed solid waste management plans. Insufficient attention to public relations may not have been the only factor forcing alteration of these plans, but a sound case can be made that better public information and education efforts would have eliminated a major stumbling block.

For some reason, people always tend to assume the worst. If a waste disposal facility is going to be located in their neighborhood, they

assume it will be a property-value-lowering dump. If a hazardous waste is to be disposed of in their vicinity, they assume that this will constitute a lasting health hazard. Some segment of the public, be it large or small, will be aware of solid waste management plans whether there is a well thought out communication effort or not. What is needed is an information program that raises awareness in an atmosphere of fact and understanding. Otherwise, awareness still grows but in a climate of rumor, misinformation, distrust, and emotional overreaction. Through a program of survey-based research and communication, public awareness and support can usually be secured.

Cost Comparison For Attitudinal Research

A survey-based research and communication effort may sound like an expensive approach. But the cost of implementing this approach should be balanced against the costs if public support is not obtained: construction delays, cancellation of plans, costly hearings, and wasted planning expenditures. Similarly, the public awareness cost must be balanced against the probability of controversy disrupting the plans.

Approximate planning costs have varied between 20 and 50 cents per person (Table 2). For the City of San Francisco (population approximately 700,000), this would have meant a planning cost of perhaps $200,000 in addition to the purchase and preparation of the proposed landfill site (full utilization of which was blocked) that cost the disposal company an additional $1,000,000 (A Study of Public Attitudes and Problems of Solid Waste Disposal, GBS Contract CPE 69-107. Prepared for USEPA, OSWMP, 1971, pp. 279-282). As mentioned earlier, the AEC spent between $7 and $8 million for planning and preparing the Lyons, Kansas, radioactive waste disposal site, only to later cancel all plans to use the site.

The $1,200,000 and the $7 and $8 million planning and preparation costs in these two cases were wasted because use of the sites was eventually lost. If 1% of the planning costs in each case had been diverted to making a social feasibility study followed by a public information campaign, chances are the remainder of the investment would not have been wasted.

Lack of experience in the use of this survey-based research and communications approach prevents an accurate prediction of what an adequate program would cost, but, based on the experience gained from this research, 1% of planning costs would be more than adequate.

These costs are believed representative and can easily be used to justify the cost of the communication approach. The other factor that must be assessed is the probability of controversy. From all indications, it appears that in the absence of a well-managed communication effort, the probability of controversy arising over hazardous wastes disposal is near 100%; the probability of controversy over waste management facilities appears somewhat lower. However, it's like playing Russian roulette: one can never be sure when contention will arise, and once it has, it is much more difficult to change people's opinions than to help form them.

The Survey-Based Research Approach

The object of the survey-based research and communication approach is to develop public awareness, approval and support for solid waste management plans. This objective is accomplished in several steps. The first task (and

TABLE 2. PLANNING COSTS

Planning area	Population	Cost	Cost/capita
Middlesex Co., N.J.	584,000	$108,000	$0.18
Cuyahoga Co., Ohio	1,700,000	319,000	0.19
Clark Co., Nev.	273,000	130,000	0.48
Santa Cruz Co., Calif.	124,000	35,000	0.28
Pierce Co., Wash.	411,000	141,000	0.34
Lane Co., Ore.	213,000	75,000	0.35

assuming the decision has been made on what methodology is to be used, i.e., incineration, landfill, deep well injection, etc.) is to identify a target audience. This task may have to be repeated several times because the target audience may change. For example, initially the target audience might be public officials and other influentials who must grant early approval. Later, emphasis would shift to environmental groups and others expected to have a high probability of concern and potential opposition. Eventually, the target audience would shift to individuals in the neighborhood affected by the waste management plans.

Secondly, as the target audience or audiences are identified, their possible reasons for opposition must be identified. Under the survey-based research concept these two tasks are accomplished through the use of carefully designed, administered, and analyzed questionnaire survey instruments. Design, administration, and evaluation of these instruments are the subjects of one of the three contracts to be discussed. Suffice it to say here that, with the contract report as a guide, these tasks are within the abilities and pocketbooks of most government authorities at the city, or higher, level.

Based on the identified target audiences and potential reasons for opposition, the next steps in this approach are to develop and sustain public awareness and support. With the background information obtained by carefully evaluating the questionnaire survey, a communications program can be designed that will provide just the education necessary for awareness and provide it in such a way that approval, support, and, if necessary, participation should result.

Research Contracts

The first of the three contracts (see page 6) consists of two reports that detail use of the survey-based research and communication approach. The other two contracts provide examples of varying degrees of use for this approach and some interesting speculation on the extent to which the approach could be used in the solid waste management field.

The GBS contract Developing Public Awareness Towards Solid Waste Problems has produced two manuals that describe in detail how to secure approval for solid waste management plans. The need for this type of material was demonstrated at the 1973 Solid Waste Management Conference in Orlando, Florida (Solid Waste Management Seminar, Sanitary Landfilling in High Water Table Areas. Sponsored by Orange County, Florida, in cooperation with USEPA, Orlando, Florida, March 26-27, 1973). In one discussion period at the conference, a sizeable number of the attending city sanitation officials agreed that one of their major problems in securing acceptance for optimal solid waste management plans developed through technical feasibility studies.

The two soon-to-be-available reports (*Planning Manual for Conducting Surveys* and *Developing and Maintaining Public Support for Solid Waste Management Systems)* provide complete detailed instructions on how to mount an education campaign that will develop and maintain favorable opinion towards solid waste management plans. The manuals detail the need for assembling baseline data; they tell of how to gather and evaluate the data, how to select target audience, and how to develop and maintain public awareness. Included are information on cost reduction, examples of public awareness programs, and detailed treatment on dealing with specific audiences. Although the manuals suggest where outside consultants might be useful, the manuals are intended to be sufficiently self-contained to permit many municipal or regional government authorities to develop a public information program entirely with their own resources, possibly with technical assistance from NERC–SWRL.

The National Analysts contract report (*Metropolitan Housewives' Attitudes Toward Solid Waste Disposal)* is an example of a portion of the survey-based research approach in action. The purpose of the research contract was to gather baseline data on housewives' knowledge about solid waste. In addition, the report assesses the apparent willingness of housewives to take an active role in solid waste management through household waste segregation or selective buying to reduce potential solid wastes.

Housewives shared a very low level of awareness of solid waste management problems but had a high level of concern for environmental problems in general. Most

significantly, the results show a very high willingness to participate in waste management. Fully 90% of the housewives surveyed expressed a willingness to separate their household waste to facilitate recycling. Further, only one housewife in 11 claimed that such separation would be difficult to carryout (Table 3).

Other results include the finding that of the housewives surveyed between 30% and 45% (depending on the product in question) would be willing to change their purchasing habits to facilitate recycling or to cut down on solid wastes. The housewives believed individuals and government both have the responsibility to solve environmental problems in general and solid waste problems in particular and that industry should share the costs.

Applying the survey-based research and communication approach in conjunction with the results of the National Analysts' report indicates that sufficient public support could be developed through an education program whereby a municipality could require household separation of solid waste. Admittedly, this would be an ambitious undertaking. But given the demonstrated public concern and a carefully managed education program, separating household wastes into a maximum of three categories should be feasible.

The third contract (Public Attitudes Towards Hazardous Waste Regional Disposal Facilities by Human Resources Research Organization) is largely based on the survey-based research and education hypothesis. A basic assumption was made that opposition should be expected towards regional hazardous waste disposal sites, and the purpose of the contract was to find out how strong that opposition might be and along what grounds it would develop. One of the report recommendations deals with the most effective approach to informing the public about proposed hazardous waste disposal sites so as to create support for the system.

One of the earliest findings of this contract was that the use of the word disposal elicited a great deal of antagonistic response. A major recommendation, therefore, is to call the sites "Regional Processing Facilities" of RPF's rather than National disposal sites.

Other results include such information as (1) people's attitudes towards RPF's, (2) how they feel about living near one, (3) how they believe an RPF would compare with a chemical plant, and (4) what additional information people would like to have about RPF's. Also contained in the contract is a profile of the types of people most and least likely to favor an RPF in their county. Those individuals not favoring RPF's were found to be generally neutral and, thus, ready to be convinced to accept an RPF by an accurate and well-managed education effort.

TABLE 3. PERCENT OF HOUSEWIVES WILLING TO SEPARATE NEWSPAPERS, GLASS, AND CANS FROM TRASH TO FACILITATE RECYCLING

Housewives willing to separate	Total	Type of dwelling		
		Detached house	Row house	Apartment
• Newspapers	94	97	95	84
• Both newspapers, glass, and cans into two containers	91	95	88	81
• Glass bottles or jars and cans	90	94	91	76
• Both from other trash, but in one container	90	95	89	77
• Not willing to separate anything	4	3	2	7

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A most important conclusion to the topic of consumerism and solid wastes is that all three studies show people are apparently prepared to evaluate solid waste management systems on the basis of the need, function, and performance of the system rather than on the basis of emotion. This situation must be presumed to be rather fragile, however, because holders of neutral or even positive opinions are also susceptible to information campaigns mounted in opposition to waste management systems. And in the absence of accurate counter information, it must be presumed that an opposition campaign could be just as effective as a campaign to build support.

Research Projects and Publications

Several studies have recently been completed; for additional information about them—and about other projects and informational materials—contact Project Officer Richard Ongerth (SWRL, NERC, Cincinnati, Ohio 45268; phone, 513/684-4484) or the distribution source or Project Officer noted.

- Assessment of Consumer Attitudes Towards Recycling of Materials, 68-03-0059, National Analysts, Philadelphia, Pa., 1972.
- A Study of Public Attitudes and Problems of Solid Waste Disposal, CPE 69-107, General Behavioral Systems, Torrance, Calif., 1971 (P.O. Albert J. Klee, 513/684-4408).

Two on-going projects are:

- A Solid Waste Public Awareness Development Program and Case Study, CPE 70-122, General Behavioral Systems, Torrance, Calif.
- Research on Public Attitudes Toward Disposal of Hazardous Wastes, 69-03-0156, Human Resources Research Organization, Columbus, Ga. (P.O. Henry Johnson, 513/684-4487).

A pertinent publication is:

- *Metropolitan Housewives' Attitudes Toward Solid Waste Disposal,* EPA R5-72-003, National Environmental Research Center, Cincinnati, September 1972, 80pp. Single copies are available from: TIO, National Environmental Research Center, Cincinnati, Ohio 45268, while the supply lasts; from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402; and from NTIS, U.S. Department of Commerce, Springfield, Va. 22151 as number PB 213 340.

Soon to be available are:

- *A Planning Manual for Conducting Surveys,* available by fall 1973.
- *Developing and Maintaining Public Support for Solid Waste Management Systems,* available by fall 1973.
- *Public Attitudes Towards Disposal of Hazardous Wastes,* available by fall 1973 (P.O. Henry Johnson, 513/684-4487).

Two 35-mm slide presentations (lasting about 12 minutes with an accompanying taped narration) will be available in midsummer 1973 at an expected cost of $20 to $30.

- Sanitary Landfill
- Waste Disposal in the Public Eye.

News of Environmental Research in Cincinnati

ADVANCED WASTE TREATMENT

May 31, 1973

U.S. Environmental Protection Agency

CONSTRAINTS TO SPREADING SEWAGE SLUDGE ON CROPLAND

G. K. Dotson

BACKGROUND

Processing organic wastes and returning them ultimately to the land is one of the most popular and far-sighted methods for dealing with them. But even sewage sludge, which is a type of waste that is obviously well suited to this type of disposal, has limiting factors that restrict its use on land. How much and how often sludge is applied to land depends in part on the objective. If the purpose of sludge spreading is disposal only, then protection of the soil is unimportant, and high application rates may be acceptable as long as water and air pollution and nuisance conditions are avoided. Reclaiming unproductive soils may also permit great leeway in regard to application rates and accumulations of sludge. But when the main objective of sludge spreading is to add fertilizer, water, and organic matter to cropland, the operating options are more limited, since the productivity of the soil and the crops must be protected. Unless otherwise stated, the following discussion pertains to constraints on the use of sludge for crop production and soil improvement in humid areas.

STATE OF THE ART

The use of sewage sludge on cropland is limited by several factors, three of which are of particular concern to environmentalists and health officials: the nitrogen content of the sludge, the concentration of metals and trace elements, and the survival of pathogens. Other factors such as public resistance, legal restrictions, unfavorable soils, or incomplete stabilization of sewage sludge may also limit methods and locations for spreading it.

Nitrogen

Nitrogen is the first sludge component to limit the rate of sludge application to land, since adding excess nitrogen to soil involves the very real risk of polluting the groundwater with nitrates.

Nitrogen Content of Sludge. Nitrogen content of sludge varies from about 2 to 6 percent, according to the composition of the sewage and the treatment of the sewage and the sludge. Digestion converts part of the organic nitrogen in raw sludge to ammonia. As part of a research grant involving sludge from the City of Chicago, the average nutrient composition of digested sludge, as a percent of dry solids, was found to be 5 percent nitrogen, 3 percent phosphate, and 0.5 percent potash. A 2-in. application of sludge to cropland will supply, per acre, 200 to 350 lb. of ammonia nitrogen, about the same amount of organic nitrogen, 250 to 450 lb. of phosphorus (of which about 80 percent is organic), and about 60 lb. of potassium (Hinesly, 1972a). A good corn crop can utilize 150 to 250 lb. or more of nitrogen per acre, and some grasses can use more.

Nitrogen Transformations in the Soil. The pathways of nitrogen in soils and the hazards they present to groundwater are difficult to predict. The processes that affect the form of nitrogen in soils (mineralization, nitrification, denitrification, immobilization, fixation, adsorption, volatilization, cation exchange, convection, dispersion, and plant uptake) may take place concurrently, and the rates at which they progress are determined largely by soil type and climate.

Mineralization (the conversion of organic nitrogen to ammonia) proceeds at variable rates depending on climate and soil conditions and the nature of the organic matter, and nitrification (the oxidation of ammonia nitrogen to nitrate nitrogen) is relatively fast in aerobic soils with favorable temperature. On the other hand, denitrification (transformation of nitrate nitrogen to nitrogen gas) takes place where free oxygen is absent or deficient and where other conditions, including a supply of carbon, are favorable for biological activity.

Microbes utilize part of the available nitrogen in soils to synthesize new cells. Ammonia ions may be fixed by organic matter and silicate clays and protected from biological attack (fixation). Volatilization of ammonia may be substantial from soils with high pH. Plant uptake varies greatly, of course, and the amount of nitrogen

removed in runoff varies with precipitation patterns and farming practices.

Nitrogen in Leachates. Ewing (1970) presented a hypothetical model indicating that only a little more than one-half inch of digested sludge per year could be applied without contributing nitrogen to leachates. But Hinesly et al. (1972a) postulated that in reality, about 10 to 15 tons of Chicago sludge per acre per year would be required to meet just the nitrogen needs of non-leguminous crops. At the Agricultural Research Center in Beltsville, Md., mixing up to 160 tons of sludge solids per acre to soils with clay subsoils did not cause nitrates to leach into groundwater at a depth of 9 ft.

Obviously, it is possible to formulate only general guidelines as to the rate that sludge can be applied to cropland without nitrate pollution of groundwater. Soil type, geology, climate, crops, and farm management are important factors in determining the fate of nitrogen added in sludge.

Metals and Other Trace Elements

Sewage sludge varies greatly in its content of potentially toxic metals, but industrial cities of all sizes tend to produce sludges that are high in metals content (see Table 1). Although sludge of domestic origin is usually lower in metals than is industrial sludge, zinc and copper are still present far in excess of the normal concentrations found in soil and, with nickel, are the metals most likely to build to toxic levels as a result of sludge spreading.

Berrow and Webber (1972), in analyzing sludge samples from 42 municipal treatment plants in England and Scotland, found that silver, bismuth, copper, lead, tin, and zinc were consistently more concentrated in sewage sludge than in agricultural soils. In a few sludges, boron, cobalt, molybdenum, chromium, and nickel were also found in higher concentrations in the sludge than in the soil, and excesses of chromium, cadmium, lead, and mercury may also be present.

Determining the permissible levels of trace elements added to soils is extremely difficult. Among the many problems, the first is to determine the amount of metals available in soils. The total amount is not important since only those trace elements that are soluble are available to the plants and cause toxicity.

Several soil characteristics interact to determine the availability of trace elements to plants. Copper, nickel, and zinc are chelated or adsorbed by organic matter, adsorbed on silicate clays, or precipitated near the soil surface. They are low in solubility and thus do not leach into groundwater. Because oxides of iron and manganese adsorb metals, maintaining oxidizing conditions in the soil tends to keep metals unavailable to plants. Neutral or slightly alkaline pH also helps to keep metals immobilized.

The second problem in establishing allowable levels of trace elements in soils is the wide difference of opinion as to what constitutes a toxic level. The British Ministry of Agriculture, Fisheries, and Food (Great Britain, 1972) recommends 500 lb. per acre as the maximum permissible accumulation of zinc or its equivalent of copper and nickel in soils in England. They consider nickel eight times and copper twice as toxic as zinc. But in the University of Illinois study, 150 tons of sludge were applied per acre over a 5-year period to corn plots without causing toxicity (personal communication, R. L. Jones, 1973). The metals added greatly exceeded the limit suggested for England. The corn yield from the maximum-sludge-treated plots equaled that from the fertilized check plot, and the quality of feed for livestock was not diminished (see Table 2).

Survival of Pathogens

The survival of pathogens in sewage sludge acts as a real constraint to sludge disposal on land. There are no records of disease caused by the use of digested sludge as a soil conditioner or fertilizer, but the matter is still of concern to many. The viability of pathogenic organisms in soil may last for only a few hours or for as long as several months (Rudolfs, 1950). The type of organism, soil moisture, temperature, and pH and the presence of antagonistic organisms in the soil influence survival time.

In a study at the National Environmental Research Center, Cincinnati, it was determined that *Escherichia coli* survived for at least 21 weeks after a single sludge application to Pennsylvania fields in the spring of 1968 (Kenner, 1971). *Pseudomonas aeruginosa* and *Salmonella* sp. were less hardy than *E. coli* under conditions of the study. Under winter conditions at Cincinnati, both indicators and pathogens lasted longer.

TABLE 1. HEAVY METAL CONCENTRATIONS IN SELECTED SLUDGE SAMPLES (ppm on dry basis)

Location	Zinc	Copper	Nickel	Cadmium
Dayton, Ohio	8390	6020	<200	830
Monterey, California	3400	720	220	<200
Tahoe, California	1700	1150	<400	40
Millcreek, Cincinnati, Ohio	9000	4200	600	< 40

TABLE 2. METALS CONTENT OF CORN (ppm oven dry basis)*

Rate of sludge application (inches per week)	Zinc	Copper	Nickel	Cadmium
	LEAF			
0	58.0	8.9	2.8	3.3
1/4	85.0	9.0	1.3	3.0
1/2	137.8	10.2	2.6	5.3
1	212.0	8.7	4.3	11.6
	GRAIN			
0	88.8	5.2	2.28	0.30
1/4	93.0	6.3	3.03	0.60
1/2	127.0	5.2	2.18	0.79
1	152.3	5.6	3.08	1.03

*Adapted from Hinesly et al., 1972 b.

If disinfection is needed, there are several methods of destroying pathogens in sludge:

- long-term storage
- pasteurizing at 70 C for 30 min
- adding lime to raise the pH to 11.5 or higher and maintaining the pH above 11.0 for 2 hr or more
- using chlorine to stabilize and disinfect sludge (the effects of the residue on soils has not been determined)
- adding other chemicals

Long-term storage of sewage has been suggested as one of the simplest methods of reducing pathogenic organisms (Berg, 1966). After storage of sludge for 30 days, fecal coliforms were reduced by 99.9 percent (Hinesly, 1972a). (Some parasites probably would persist much longer, however.)

Pasteurization by maintaining a temperature of 70 C for 25 to 30 min kills pathogens, viruses, cysts, and worm eggs (Liebman, 1967). In a study of pasteurizing digested sludge conducted at the National Environmental Research Center in Cincinnati (Dotson, 1973), pathogens were killed when direct steam injection was used in the laboratory and in a tank truck to raise the temperature of the sludge to 75 C and maintain it for 1 hr. The sludge killed bluegrass when applied to the lawn at a temperature greater than about 60 C, and the estimated cost of pasteurizing four 5,000-gal truckloads of sludge per day was estimated at $12.50 or less per ton of solids.

Liming digested or physical-chemical sludges to pH 11.5 killed pathogens in batch tests at Lebanon, Ohio. The cost of this treatment was estimated to be about $10 per ton of solids (Farrell, 1972).

Other Factors That Limit Sludge Disposal on Land

Other factors limit where sludge can be applied and the rate of application: odors, the presence of ammonia and other toxins, and public resistance. A sludge spreading plan that is developed and publicized with local residents is much more likely to be received with enthusiasm that one that is planned and implemented by a city.

WHAT'S NEEDED

Much research needs to be done, and a number of steps should be taken to mitigate or eliminate the factors that limit sludge spreading on cropland. With regard to the nitrogen content of sludge, management options (such as removing nitrogen from sludge or leachates) should be exercised, and additional management techniques should be developed. Of course, simply adding excess nitrogen to soil does not necessarily mean that nitrates will enter a water table. The gradual accumulation of organic matter, which will release nitrogen as it decomposes, may well be the real factor that limits the sludge load.

There is a dearth of information concerning the fate of heavy metals applied to soils. Many combinations of soil types, plant species and varieties, and climates have been considered in toxicity reports, but the concentrations of metals in the soils and plants have not been recorded.

Furthermore, many of the toxicity studies have involved excess of only one or two elements. The interactions of many trace elements in sewage sludge are not fully understood. Greenhouse and other studies at the University of Illinois (Hinesly, 1972a) have confirmed that there are both synergistic and antagonistic interactions between metals that affect the uptake and translocation within plants.

The long-range effect of sludge applications that contain a surplus of nutrients and trace elements remains to be determined. There is inadequate definitive information available now to set precise guidelines for sludge application to soil based on its metals content. Long-term field studies such as those at the University of

Illinois are needed for various combinations of crops, soil types, and climates. Use of certain benchmark or indicator crops by all those doing research on the effects of metals would permit correlation of the results.

Pending the establishment of guidelines for permissible additions of trace elements in sludge, some precautions could be taken to prevent soil pollution with high rates of sludge application or prolonged applications at lower rates. Regular testing of crops and soils should be adequate to forewarn of toxic accumulations. Liming to control pH and maintaining oxidizing conditions and high levels of organic matter in the soil will help to keep metals immobilized.

The disease hazard presented by surviving pathogens in sewage sludge can be greatly reduced or eliminated by:

- employing good soil and water conservation practices to prevent erosion from sloping land that has been spread with sludge;
- percolating water through at least 5 feet of unsaturated soil to remove pathogens; and
- disinfecting the sludge by one of the methods discussed previously.

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CAM–1: USING ENZYMES TO DETECT INSECTICIDES

John E. Brugger*

INTRODUCTION

The rapid monitoring and accurate detection of certain cholinesterase-inhibiting substances in watercourses are critical. These materials, which include insecticides of the organophosphate and carbamate types (Azodrin, DDVP, dimetilan, malathion, parathion, paraoxon, and Sevin), interfere with physiological and neurological functions by inhibiting the action of cholinesterase-type enzymes. They are toxic to living things, particularly to humans.

The development of CAM-1, a fully engineered prototype model of a system for using enzymes to detect organophosphate and carbamate pesticides in water, represents a significant technological advance in the field. The device is the first instrument to sucessfully use an immobilized enzyme product for automatically monitoring water supplies for the presence of cholinesterase-type inhibitors. CAM-1 is sensitive enough to prevent the poisoning of humans and animals by a wide variety of organophosphate and carbamate insecticides. Although it was specifically designed to monitor the concentration of these types of insecticides in water supplies, the device can also be used to check the quality of industrial plant effluents and to detect spills of the types of pesticides to which it responds.

A cholinesterase is an enzyme that causes the hydrolysis (splitting) of esters of choline. Cholinesterase is essential to the proper functioning of the human nervous system. Certain organophosphates (which are produced by the reaction of phosphoric acid and alcohols) inhibit or are antagonistic to action of the enzyme cholinesterase. Thus, CAM is an acronym for "cholinesterase antagonist monitor," and its action can be regarded as that of a toxicity meter for certain materials.

Previous attempts to use cholinesterase-type enzymes for pesticide detection generally depended on adding the enzyme to the suspected water and then determining whether the enzyme retained the capacity to hydrolyze a material (substrate) that was subsequently added. Frequently, the determination was made by spectrophotometric means. The procedure was time-consuming and unsuitable for the rapid alarm required to signal the presence of toxic levels of organophosphate pesticides in water supplies. Furthermore, the enzymes and substrates were moderately costly and were required in considerable quantities.

CAM-1 was developed by the Midwest Research Institute (MRI) in Kansas City, Missouri, under EPA's Hazardous Materials Spills Research Program. The project (EPA Contract No. 68-01-0038) was sponsored by the Edison Water Quality Research Laboratory of the National Environmental Research Center in Cincinnati, Ohio.

In 1972, CAM-1 received national recognition at the IR-100 annual competition, where it was selected from several thousand entries as one of the 100 most significant advances in applied science and technology. The device was included in the month-long IR-100 display at the world-famous Museum of Science and Industry

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in Chicago. Requests for further information about CAM-1 have been received not only from interested parties in the United States, but also from scientists and engineers in 29 foreign countries.

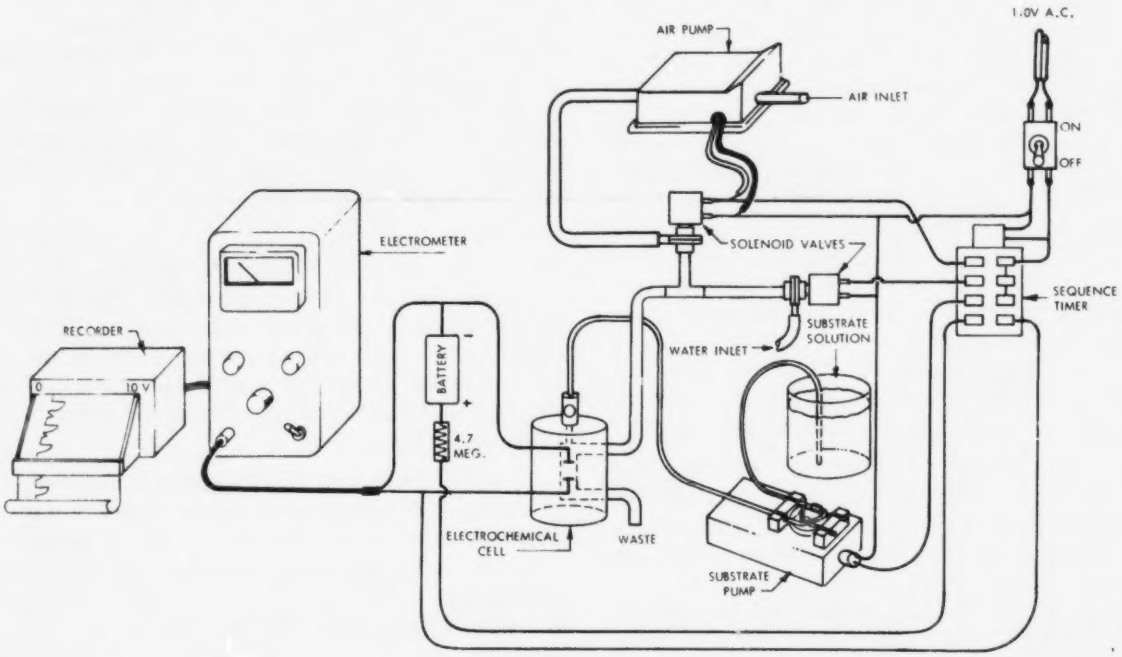
DESIGN AND OPERATION OF CAM-1

Two technological advances were needed to accomplish the creation of the CAM-1 system: (1) development of techniques for bonding an enzyme to a carrier material so that the enzyme is active, conserved, and readily available, and (2) the development of some rapid, convenient, accurate method for detecting hydrolysis of the substrate. A breakthrough came with development of techniques for bonding an enzyme to a carrier; MRI bonds the enzyme either to cotton or to polyurethane foam. The process roughly resembles dyeing with a mordant. MRI developed an in-place, electrochemical method for determining the extent or degree of hydrolysis, which is an inverse measure of the inhibition of the enzyme (or, consequently, of the toxicity of the water being tested).

After these two major obstacles had been overcome, a flow-through system could be engineered. In this system, water suspected of containing organophosphates is passed through a pad dyed with the enzyme.* The water flow (500 ml/min) is diverted, and a small amount of substrate solution (1 ml) is added to the pad. When the enzyme has not been inhibited by the toxic materials in the water, the substrate will be hydrolyzed. When there has been an inhibition of the cholinesterase, however, the rate of hydrolysis of the substrate, as well as the quantity of material hydrolyzed during the operating time period, will decrease.

The critical element of the CAM-1 design is a pad of immobilized cholinesterase, which is sandwiched between perforated platinum electrodes. The electrode unit is about 8 mm thick and 1 cm in diameter. Water is pumped through the pad for 2 min; during the third minute, air and an enzyme-active reagent or substrate solution is forced through the cell (the enzyme is equine serum cholinesterase (I.V.B. 3.1.1.8), and the substrate is 2.5×10^{-4} M butyrylthiocholine iodide in 0.08 M TRIS buffer at pH 7.4). Finally, during the last half minute of the complete 3-min cycle, a battery is connected across the platinum electrodes and a

*Pesticide in the water reacts with (and thus inactivates) immobilized enzyme molecules to an extent that is proportional to the quantity of pesticide passed through the cell and at a rate that is proportional to the concentration of the pesticide in the water.



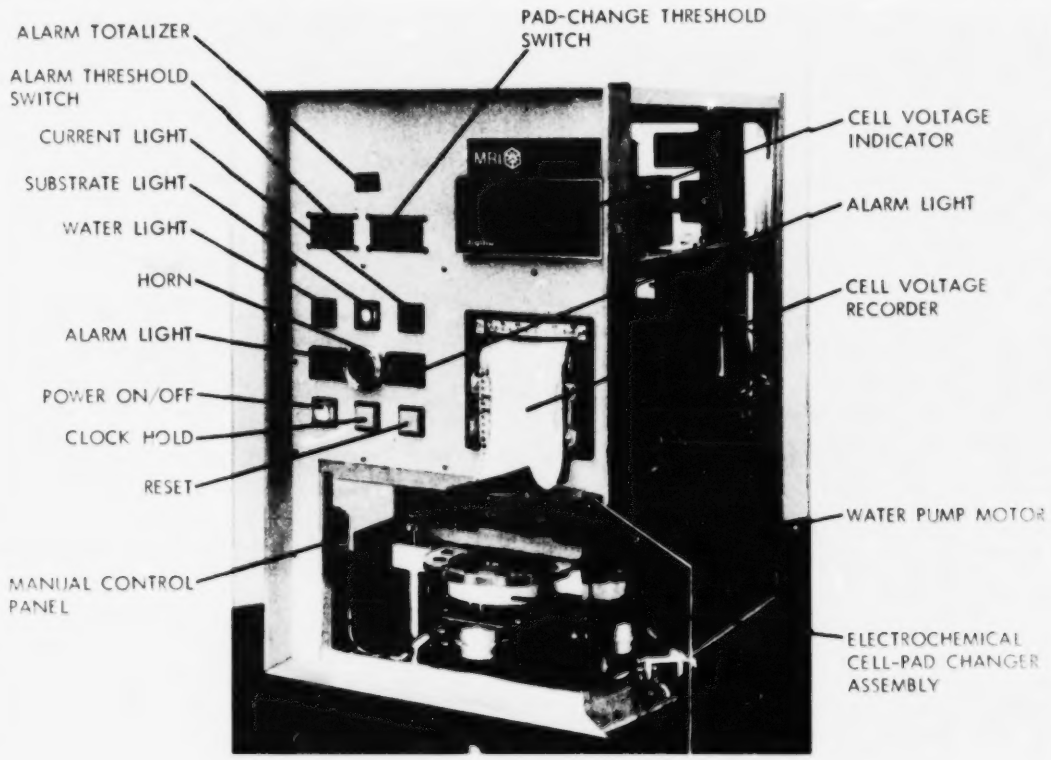
small current (2 μA) flows through the cell. When the substrate is being hydrolyzed at the maximum rate (that is, when the cholinesterase has not been inhibited by toxic substances in the water), the voltage across the cell will be significantly lower than when the enzyme has been inhibited. The voltage registers on a digital voltmeter and on a small strip-chart recorder. (The normal voltage for a fresh pad is about 100 mV; the voltage across an inactivated pad is about 500 mV.)

The explanation for the voltage change has not been sought in detail, but the change does not arise from a mere alteration in conductivity. There is evidence that both a redox potential change and a depolarization effect are involved. On hydrolysis, the substrate produces a hydrosulfide, which is readily electrooxidized to a disulfide. The redox potential of such a hydrosulfide-disulfide half-cell is of the proper order. As the immobilized enzyme becomes inactivated, the concentration of hydrosulfide available for oxidation is decreased, and the potential of the couple increases toward that of the oxygen electrode potential.

The electronics are designed so that a previous cell voltage reading can be stored in the memory of a small, built-in computer and compared with a new voltage reading. When the new voltage is greater than the previous voltage by a preset value (which can be dialed into the CAM-1 device), an alarm sounds.

With time, the enzyme pad loses some of its activity, particularly because of inactivation by toxic substances, but also as a result of the slow washing out of the enzyme. In normal operation, a pad is good for a day. A pad-change voltage can be dialed into CAM-1, so that when the voltage exceeds a preset value, the cell is automatically opened and the pad changed. The device holds ten new pads. Thus, CAM-1 operates for several days without attention, unless organophosphates occur in the test water in such concentration and duration that the pad supply is used up.

CAM-1 is designed so that it can be operated in tandem with a second unit, but half a measurement cycle (1½ min) out of phase. This arrangement reduces the minimum alarm time



and provides, in addition, complete sampling of the water; there is no "dead" time. The arrangement with two units in tandem is self-confirmatory.

In a limited series of laboratory experiments, CAM-1 consistently gave an alarm at the concentrations of pesticides shown in Table 1. The alarm threshold level was set at 15 millivolts, but a detection limit 2 or 3 times smaller (5 millivolts) can certainly be used with the existing device.

TABLE 1. ALARM RESPONSE OF CAM-1 TO SELECTED INSECTICIDES

Type of insecticide	Response concentration ppm	LD_{50}, rats mg/kg
Organophosphate:		
Malathion	16	1,640
Parathion	5	56
DDVP	1	56
Paraoxon	0.1	4
Carbamate:		
Sevin	50	560
Dimetilan	10	64

Toxicities are given for reference. A rough correlation exists between toxicity and the CAM-1 response levels; but it should be noted, for example, that a rat weighing 1 kg would have to imbibe more than 10 liters of water with a parathion concentration of 5 ppm to accumulate a toxic dose (56 mg/kg of body weight) of the pesticide (5 ppm = 5 mg/liter = 5 mg/kg water).

FUTURE DEVELOPMENTS

The next steps in the development of CAM-1 will be to determine whether any nontoxic materials give alarm signals and to measure the actual threshold limits for a wide variety of pesticides. In principle, the CAM-1 system could also be developed to use enzymes other than cholinesterase. The following represent a few examples of enzymes and the substrates that are antagonistic to their action: catalase (cyanides, azides), urease (fluorides, formaldehyde), lipase (aldrin, lindane), hexokinase (2,4-D and 2,4,5-T), and cytochrome oxidase (cyanides).

CAM-1 can be produced in a simplified, more portable version that will be suitable for rapid detection of cholinesterase antagonistic pesticides under field conditions.

ACKNOWLEDGMENT

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SOLID WASTE RESEARCH

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PLASTICS AND INCINERATION

Robert C. Thurnau and Nancy S. Ulmer*

BACKGROUND

As plastic sales continue to soar in the United States (11 million metric tons, or 24.2 billion lbs in 1972[1]), the amount of discarded plastic waste also increases and the question of its impact on the environment emerges. About 75 percent of the plastics produced are discarded in a relatively short period of time. The unbreakable shampoo bottle, food wraps and packages, and the outer liner of disposable diapers are examples of the typical examples of plastic wastes being introduced into the municipal solid waste stream.

In terms of quantity, plastics comprise a very small part of the total municipal waste produced each day. Recent estimates suggest that plastics represent about 2 percent of all municipal solid waste, a figure that is projected to increase to 3 percent by 1980. The problems associated with the disposal of plastic wastes are, however, proportionately larger and thus merit additional investigation.

The problems associated with the incineration of plastics can be divided into two broad areas: toxic and noxious emissions generated during open and uncontrolled burning and possible damage to incinerators from corrosion. Currently, about 90 percent of the municipal solid waste is disposed in landfills. If the landfill is operated efficiently, open burning is eliminated along with noxious and toxic emissions. Recent surveys[2] have shown, however, that only 6 percent of 1,800 landfills studied can be considered sanitary and that about 75 percent of the remaining have open burning on site. If that part of the waste burned in open dumps is added to the 10 percent burned in incinerators, the amount of plastic waste being combusted is not insignificant.

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STATE OF THE ART

The Federal Government has initiated several research projects to determine the nature and magnitude of the problems associated with the disposal of plastics by incineration. Specifically, the investigations were designed to determine the thermal decomposition products of plastics and the toxic and corrosive action of the decomposition products.

Combustion Products from Incinerating Plastics

In 1969, Boettner at the University of Michigan (supported by Solid Waste Research Grant EP-00386, awarded by USEPA, NERC-Cincinnati) investigated the combustion products from the incineration of plastics. The thermal degradation and combustion product analyses were undertaken to provide scientists and engineers the information needed to design and operate incinerators with maximum efficiency and minimal maintenance and pollutant emission. The investigators also hoped to identify among the products of incomplete combustion those materials that were potentially recoverable for their fuel or crude chemical value and those products that would be acutely toxic to anyone exposed to uncontrolled or accidental burning of plastics.

In the February 1973 final report of this study,[3] Boettner et al. presented the results of their studies of polyethylene, polyvinyl chloride, polystyrene, polypropylene, polysulfone, polyurethane, polyimide, acryonitriles such as Barex* and Lopac, phenol and urea formaldehydes, polycarbonate, polyphenylene oxide, and polyester. A thermal analysis (DTA and/or TGA) of each plastic was first performed to determine the temperatures at which chemical and physical changes occurred in the sample.

In the presence of air or air plus oxygen, 1- to 3- g samples of each plastic were heated at a controlled rate from 5 to 50 cc per min. The compounds that were liberated within the temperature ranges previously determined to be significant by thermal analysis were identified, characterized, and/or quantitated.

When plastics containing carbon and hydrogen (e.g., polyethylene and polypropylene) or carbon, hydrogen, and oxygen (e.g., polystyrene, polycarbonate, polyphenylene oxide, and polyester) are combusted completely, carbon dioxide and water form. In these studies where combustion was purposely incomplete, carbon monoxide was the major toxicant formed along with gaseous and condensed hydrocarbons. The investigators noted that the fuel or crude chemical value of the condensate was significant but they suggested that the aromatic polymers in the condensate might be a source of polycyclic hydrocarbon pollution.

The nitrogen-containing plastics (e.g., polyurethane, polyimide, acrylonitrile-based Barex and Lopac, and urea and phenol formaldehydes) normally yield nitrogen oxides, carbon dioxide, and water on complete combustion. The investigators reported that incomplete combustion produced hydrogen cyanide, cyanogens, nitriles, and ammonia in addition to hydrocarbon gases. The production of cyanide and ammonia generally increased as the completeness of the combustion decreased. The hazards associated with the open or accidental burning of such plastics were emphasized in the report.

*Mention of a commercial product does not imply endorsement by the U.S. Government.

Carbon dioxide, water, and acid gases (hydrogen chloride or fluoride) or sulfur dioxide normally form on complete combustion of plastics containing a halogen (e.g., polyvinyl chloride) or sulfur dioxide (e.g., polysulfone). Boettner reported that incomplete combustion of these plastics produced organic halogen and sulfur compounds that could cause air pollution, incinerator corrosion, and toxicity problems.

Toxicity Studies

The question of the potential physiological hazards associated with exposure to the products of burning plastics was raised in the 1960's, when the use of plastics in the manufacture of commercial and household products began to increase. In 1967, Zapp[4] reported that rats exposed to the pyrolysis products of polyurethane foam revealed pulmonary congestion and edema. A short time later, Waritz and Kwon[5] noted that exposure to Teflon pyrolized at 450 C produced acute pulmonary hemorrhage and edema in rats. Coleman[6] proposed that carbonyl fluoride might be the major toxic product of Teflon degraded at 550 to 700 C. McFarland and Leong[7] observed death in animals exposed to polyurethane decomposition products and suggested that acute asphyxia from occlusion of the upper right respiratory tract had occurred. Similar deaths observed in animals exposed to polyurethane-nylon degradation products were attributed, however, to a slowly developing pulmonary edema. McFarland and Leong also reported the hazards associated with the exposure of animals to the products of epoxy resins.

In 1969, Cornish and Abar[8] published the results of their investigations of the toxicity of the pyrolysis products of vinyl materials. This research was supported in part by Public Health Service Grant UI-00485 from the National Center for Urban and Industrial Health. They combusted 1- to 2- g samples of PVC polymers and formulations in a stream of air by gradually raising the temperature to 600 C. Animals were exposed to the effluent air stream after it was diluted to twice its original volume. The deaths, observed in 50 percent of the animals, were attributed to carbon monoxide. Carboxyhemoglobin levels correlated well with

the amount of plastic combusted. Little lung damage was noted in the histological studies. Pulmonary edema and interstitial hemorrhage developed when oxygen was added to the air stream to prevent deaths from carbon monoxide. Some animals exposed to high levels of the pyrolysis products of vinyl chloride-vinyl acetate copolymers also revealed focal edema and intra-aveolar hemorrhage. Exposure to polyvinyl formulations containing additives and inert materials appeared to produce less toxic effects.

In 1969, additional toxicity studies were initiated by Heimburg at Syracuse University (Solid Waste Research Grant EP-00304, awarded by USEPA). In the final February 1972 report (Incineration of Plastics Found in Municipal Wastes,[9]) Heimburg described the exposure of plants and animals to the combustion products of polyethylene, polypropylene, polyurethane, and the acrylonitrile-based polymers. He found that improper combustion conditions generated increased amounts of soot, carbon monoxide, ammonia, nitrogen oxides, and cyanides. The establishment of optimum combustion conditions eliminated these products. He also reported that the combustion of PVC yielded hazardous and corrosive emissions regardless of the combustion conditions.

Corrosion Studies

The previously cited works dealt with thermal degradation products and their physiological effects on plants and animals. The second area of concern involves the corrosion problems experienced by municipal incinerators. Battelle Memorial Institute was commissioned to initiate a study into the metal wastage in municipal incinerators.[10] The goal was to determine the mechanism of corrosion and then take steps to circumvent or inhibit the reactions responsible for the decay.

Special probes were designed and constructed so that the metal to be exposed was repeated at designated positions giving a temperature profile effect of corrosion in addition to showing the effect of the gases on the metal itself. Fifteen probes were placed in several incinerators and allowed to experience combustion gas conditions for 10,426 hr. The average time per probe test was 695 hours and the tests were conducted from December 1969 to January 1972.

A sequence of reactions explaining the mechanism of corrosion was developed (see Figure 1). Essentially the mechanism is simply a reaction between a chloride species with the iron and a sulfur species with the iron. Subsequent oxidations change the iron to the common ferric oxide. (A crossection of the deposit can be found in Reference 10, Figure 20, p.54.)

The Society of the Plastics Institute commissioned several investigators to look at the effects of the incineration of plastics.[11] They found that although poorly operated incinerators have smoke and odor problems because of incomplete combustion, these can be corrected. The burning that occurs in open dumps, however, cannot be optimized; thus soot, unburned hydrocarbons, toxic gases, and other hazardous compounds can be emitted into the environment if the burning is uncontrolled. The responsibility for these emissions is usually placed on the community; however, the question exists of whether the manufacturers should plan and design with the environment in mind.

The problem of corrosion in municipal incinerators has not been taken seriously enough. The plastics industry has stated that properly designed and operated incinerators show no new phenomena in regard to corrosion from plastics.[12] There are, however, numerous operators of modern, efficient incinerators who experience corrosion problems and attribute the majority of their problems to plastics.

CURRENT RESEARCH

The National Environmental Research Center in Cincinnati is still studying the role that plastics play in the thermal degradation of municipal solid waste. Specifically, the work is oriented toward verifying the question: can any changes in the corrosion rate be attributed to plastic after varying the chloride-containing plastic and holding other incinerator conditions as constant as possible? This type of study is currently underway, and preliminary results for chloride concentrations of 0, 0.5, 1.0, and 2.0 percent by weight show that:

- For low alloy steels, the corrosion rates are markedly affected by PVC content in the refuse.
- For low alloy steels, a small increase in PVC concentration produces a sharp increase in the corrosion rate.

• For low alloy steels at temperatures of 900 F or above, the corrosion rate is a linear function of the PVC concentration.

• For high alloy steels, the corrosion rate at low operating temperatures is essentially unaffected by PVC concentration but does increase when the temperatures are raised.

• For high alloy steels, stress corrosion cracking is observed, with the major mode of attack being pitting.

Figure 2 shows the relationship between the corrosion rates of one low alloy steel and the amount of PVC added to refuse.

WHAT'S NEEDED

The controversy over plastics and the role they play in environmental problems will continue. The question of economics and the utility of plastics will have to be balanced by the effects they have on the environment.

The most important area of concern should be the emissions from open burning dumps and incinerators. Earlier studies showed that inhaling concentrated samples of plastic combustion products was harmful and toxic, but the effect of breathing diluted, low-level concentrations for long periods of time is unknown. The determination and control of threshold concentrations of plastic in refuse should be studied.

Additional investigation into the mechanism of corrosion should also be initiated. The role of sulfur should be studied and quantified, and work should be done on inhibiting corrosion through metal pretreatment or coatings.

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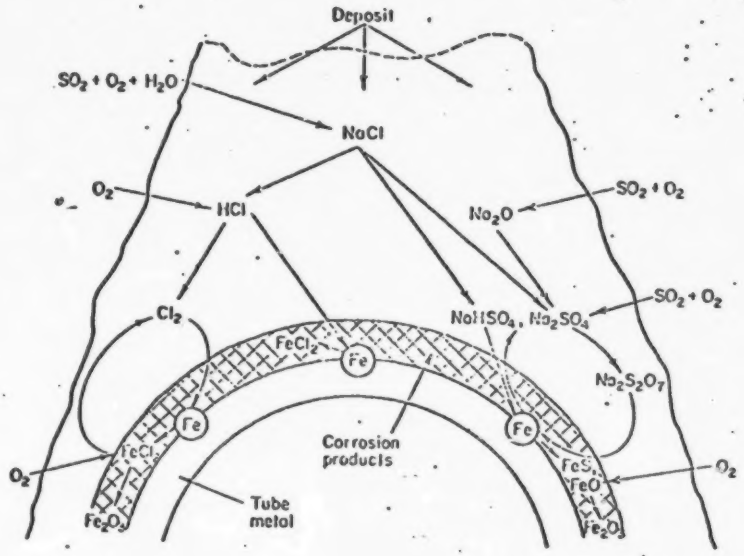

FIGURE 1. SEQUENCE OF CHEMICAL REACTIONS EXPLAINING CORROSION OF INCINERATOR BOILER TUBE (Ref. 10, p.80).

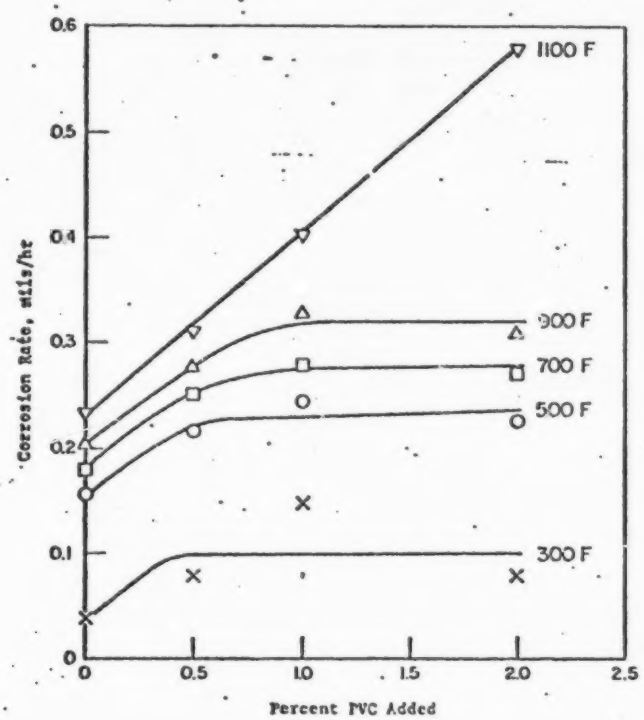

FIGURE 2. CORROSION RATE OF A106 STEEL AT VARIOUS TEMPERATURES VERSUS PERCENT PVC ADDED TO REFUSE (Ref. 12, p.12).

News of Environmental Research in Cincinnati

U.S. Environmental Protection Agency

EDISON WATER QUALITY

August 10, 1973

USING POROUS PAVEMENT TO CONTROL RUNOFF

Hugh Masters*

BACKGROUND

Pollution from sewer overflow is currently a problem for approximately 18 percent of the Nation's population served by combined sewers. During storms, interceptor sewers are too small to handle the volume of flow generated, and thus, the major portion of stormwater and domestic sewage flows directly into receiving watercourses. These flows carry with them as much as 40 percent of the year's production of suspended solids, putrescible organic matter, and bacteria. Such materials tend to settle at the bottom of a sewer during dry weather periods, but in the combined sewer overflow, they are swept up and out, untreated, to surrounding watercourses. The untreated pollutants contribute significantly to the degradation of surrounding waters. The feasibility of utilizing porous pavements to alleviate combined sewer overflow and stormwater discharge pollution is under study by the Storm and Combined Sewer Technology Branch at the Edison Water Quality Research Laboratory. By allowing stormwater to percolate into the soil, rather than to fill the sewer system, porous pavement could prevent a major portion of this overflow problem.

CHARACTERISTICS

Lab tests show that porous pavement is highly permeable to water. Up to 70 in. of water per hour can flow through a 2½-in.-thick sample (see Figure 1). Unlike normal asphalt concrete

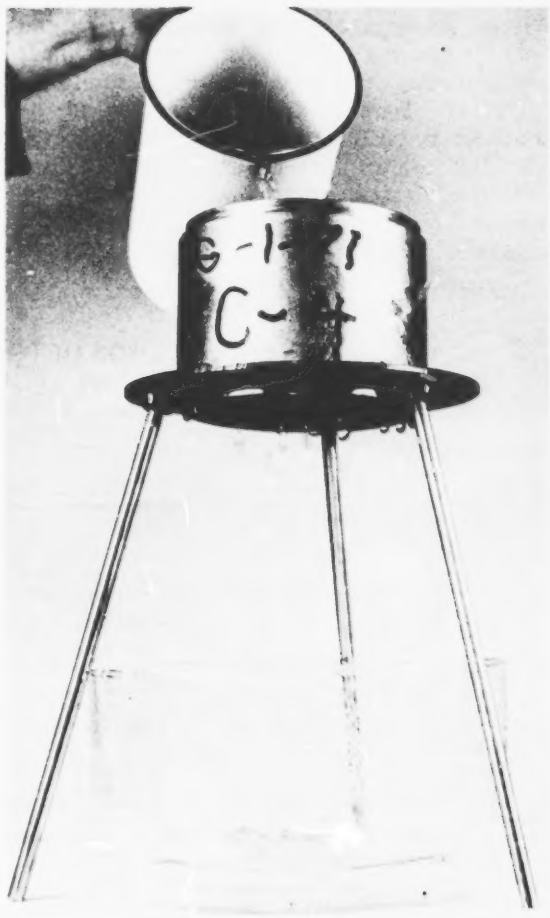

Figure 1. Water flowing through a 2½-in.-thick sample of porous pavement.

*Mr. Masters is a Sanitary Engineer with the Storm and Combined Sewer Technology Branch in Edison, New Jersey (201-548-3510).

paving, porous pavement omits fine aggregate particle sizes (only 0 to 3 percent passes through a 200-mesh sieve, compared with 15 percent for normal paving). Thus, enough pores are present for water to drain readily, yet the material retains satisfactory strength and durability.

Porous pavement shows good mechanical stability (Marshall test) and high oxidative resistance (exposure to air at 150 F for 8 weeks caused no untoward effects). Some 265 freeze-thaw cycles caused no change in mechanical stability. Moreover, bacteria seem likely to flourish underneath this type of pavement and would probably degrade substances washed through.

COST ADVANTAGES

The use of porous pavement could substantially reduce the cost of sewer systems. Where inadequate storm sewers or natural drainage systems already exist, porous pavement could alleviate the need to provide additional capacity. Where sewers are yet to be constructed, such pavement would permit the installation of a smaller storm drainage collection system than would otherwise be needed.

A recent study[1] conducted by the Franklin Institute Research Laboratory (FIRL) under contract to EPA indicated that reducing the size of storm sewers or eliminating them entirely in some cases would be the major savings associated with the use of porous pavement. The study estimates that for all but the cheapest paving uses, the cost of porous pavement would be equal to or less than conventional pavement with gutters. The cost of porous pavement used in inexpensive, residential street paving was projected to be $6.35 per sq yd, compared with $7.20 for conventional paving with storm drainage. Maintenance costs were calculated to be comparable or less than those for conventional pavements.

During the course of the FIRL study, a variety of conventional and unconventional materials were investigated. The most promising ones were tested to determine their physical and

[1]Investigations of porous pavements for urban runoff control. Thelen, E., W. C. Grover, A. J. Hoiberg, T. I. Haigh. U.S. Environmental Protection Agency, Washington, D.C. Report No. 11034DUY03/72, GPO, $1.25.

TABLE 1. COST COMPARISON OF POROUS PAVEMENT AND CONVENTIONAL PAVEMENT WITH STORM DRAINAGE

Type of pavement	Porous pavement		Conventional pavement	
	Cost range ($/y²)	Average cost ($/y²)	Cost range ($/y²)	Average cost ($/y²)
Parking lot	6.32 - 6.40*	6.36	3.65 - 5.81	4.73
Residential street				
Low-design	6.33 - 6.37*	6.35	4.80 - 9.60	7.20
High-design	6.19 - 6.56	6.38	8.35 - 12.10	10.23
Business street				
Suburban development	6.65 - 6.99	6.38	6.90 - 9.90	8.40
City	6.99 - 8.32	7.66	14.20 - 22.20	18.20
County road	6.01 - 6.87	6.44	7.24 - 13.23	9.20
Highway				
Two-lane	6.80 - 7.92	7.36	8.54 - 20.45	14.50
Four-lane				
Asphalt	8.16 - 8.79	8.48	16.36 - 31.40	23.88
Concrete	8.23 - 9.04	8.64	17.76 - 33.90	25.83
Playground	4.35 - 4.36*	4.36	3.90 - 5.20	4.55

*Range reflects differences in excavation costs.

economical feasibility as porous pavement materials. An open-graded asphalt concrete was selected as the most suitable material because of its superior physical characteristics, its low cost, and its ability to be laid by conventional paving methods. Recent developments in porous Portland Cement technology may make it a suitable candidate for porous pavement material also.

Feasibility investigations for pavements other than roadways indicated that artificial turfs did not have adequate permeability as porous playground pavements. A resilient, porous surface of adhesively bonded chopped rubber intended for playground use exhibited suitable physical characteristics but was judged too expensive for most uses. Similarly, pavements assembled at the site from factory-made components such as bricks or honeycombs appear to be uneconomical.

TESTING PROGRAM

EPA's Storm and Combined Sewer Program has taken the next step in the development of porous pavements: to pave several acres in different locations to test the material in actual use. Two potential projects will demonstrate this use of porous pavement in southern areas.

Open-graded asphalt and Portland Cement Concrete test areas in these projects will be compared with conventional pavement with a drainage system. Specific project objectives will be to determine the beneficial aspects of employing porous pavement to reduce or prevent stormwater runoff, thus decreasing stream pollution but increasing groundwater recharge.

Another objective is to determine the fate of pollutants that filter through the porous material by providing an under-drain system to collect filtered stormwater for chemical and biological analysis. This information is extremely important to have because of potential groundwater pollution from stormwater infiltration and possible plugging of porous pavements by nondegradable pollutants.

Other important considerations in the studies will be to determine a suitable base material for use with porous pavements; to examine in situ its physical and chemical characteristics versus time; to take a look at its safety benefits with respect to elimination of flooding, increased visibility, and reduction of skidding from wet pavement; and to determine the economic benefits of porous pavements.

Another important aspect of the projects will be to demonstrate the efficiency of vacuum cleaning streets to reduce the pollution load from stormwater runoff. A recently completed EPA research project entitled "Water Pollution Aspects of Street Surface Contaminants," monitored by the Storm and Combined Sewer Program showed that most pollutants (approximately 75 to 100 percent) are associated with particles smaller than 2,000 microns. Existing street-cleaning equipment has a low efficiency for removing particles of this size. A street-cleaning vacuum machine specially designed to have a high cleaning efficiency will be used to clean one conventional pavement area and one porous pavement area. This test will allow a demonstration-comparison of the use of highly efficient street cleaning equipment to reduce pollution related to stormwater runoff for both conventional and porous pavements. Also, it will determine whether or not street cleaning will prevent the plugging of porous pavements.

CONCLUSION

In summary, the Storm and Combined Sewer Program anticipates a practical solution to several of its program needs through the successful demonstration of porous pavements. The major needs are relief from flash flooding, safer roads, partial elimination of combined sewer overflows and stormwater discharges, groundwater recharge, and preservation of vegetation (trees and shrubs near conventional pavements often starve because of dry soil, but they will grow in a parking lot with porous pavement). In the future, porous pavements may well become the preferred material for many pavement uses.

Reports recently submitted to the National Technical Information Service, Department of Commerce, Springfield, Virginia 22151; including the PB order number and cost:

"Single Cell Proteins from Cellulosic Waste," EPA-6702-73-02., PB 221 096, cost $5.45.

"Utilization of Bark Waste," EPA-670/2-73-005, PB 221 876, cost $6.00.

"Investigation of Corrosion Deposition Phenomena on Gas Turbine Blades," EPA-670/2-73-006, PB 221 095, cost $3.75.

"Biological Conversion of Animal Wastes to Nutrients," EPA-670/2-73-009, PB 221 171, cost $4.85.

"Preparation and Evaluation of Activated Carbon Produced from Municipal Refuse," EPA-670/2-73-010, PB 221 172, cost $5.45.

"Acid Hydrolysis of Cellulose in Refuse to Sugar and Its Fermentation to Alcohol," EPA-670/2-73-011, PB 221 239, cost $5.45.

"An Analysis of the Abandoned Automobile Problem," EPA-670/2-73-013, PB 221 879, cost $6.00.

"A Studyof Hazardous Waste Materials, Hazardous Effects and Disposal Methods, Volume I," EPA-670/2-73-014, PB 221 465, cost $10.60.

"A Study of Hazardous Waste Materials, Hazardous Effects and Disposal Methods, Volume II," EPA-670/2-73-015, PB 221 466, cost $12.50.

"A Study of Hazardous Waste Materials, Hazardous Effects and Disposal Methods, Volume III," EPA-670/2-73-016, PB 221 467, cost $10.60.

Reports currently available from the Technical Information Office, NERC-Cincinnati:

"Physical, Chemical and Microbiological Methods of Solid Waste Testing," by D. F. Bender, M. L. Peterson, and H. Stierli, editors. EPA-6700-73-01, May 1973; also available from the National Technical Information Service as PB 220 479, cost $6.75.

"Procedures for Radiochemical Analysis of Nuclear Reactor Aqueous Solutions," by H. L. Krieger and S. Gold. EPA-R4-73-014, May 1973.

"List of Environmental Research Publications," EPA-670/9-73-004, July 1973.

Algae posters - set of six - reprinted from "Algae in Water Supplies," by C. M. Palmer, 1962.

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PROGRAM COORDINATION OFFICE

(Office of Director)

August 31, 1973

RELATING SOCIO-ECONOMIC VARIABLES TO TECHNOLOGY FOR ENVIRONMENTAL MANAGEMENT

Robert M. Clark and Haynes C. Goddard*

BACKGROUND

A traditional approach to solving environmental problems is to use technology to provide immediate solutions and to ignore the behavioral, social, and economic characteristics of the population being served. Such an approach is often justified by rationalizing that today's problems must be solved today and that tomorrow's problems can always be left to the research community. Often, however, the researcher as well as the practitioner is under intense pressure to produce a better piece of hardware or an analytical technique that will provide at least a short-term solution. This continual emphasis on stopgap measures means that practitioners and researchers must constantly respond to a series of crises rather than plan systems that can prevent their occurrence. One way to avoid this crisis orientation would be to determine how socio-economic variables affect technology for environmental management and to structure technological research accordingly so that it anticipates rather than responds to need.

The National Environmental Research Center in Cincinnati (NERC) has a limited but significant program designed to incorporate socio-economic variables in the planning for future research. The program is conducted throughout the NERC laboratories and provides significant input to the Agency's overall operational plan. This article provides an example of the advanced thinking required to determine the influence of socio-economic variables on technological choice for environmental management. In this case, urban population dynamics are examined with regard to their impact on the choice of solid waste disposal systems. A more detailed version of this paper was presented by the authors at Wright State University's Symposium on Solid Waste in the Extractive Industries held June 11-15, 1973.

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THE EFFECTS OF DECENTRALIZED URBAN ACTIVITY

In 1960, about 70 percent of this country's population resided in areas classified as urban by the U.S. Bureau of Census. In 1970, this percentage had risen to 73 percent, and it is estimated that this figure will reach 79 percent by 1980[1]. These statistics demonstrate the importance of urban areas in the United States and emphasize the continuing trend for more and more Americans to live and work in an urban environment. However, in conjunction with the trend away from rural life (which would seem to imply the growth of large central cities) is a trend toward suburbanization and the spread of urban activities over a larger and larger area. Since many environmental problems are associated with heavily urbanized areas, this spreading or decentralization of economic activity is making environmental management increasingly difficult and costly.

The spread of urban activity decreases the densities of residential and commercial land use and increases the area over which production and consumption residuals must be managed. For example, water and wastewater treatment

systems have significant economies of scale associated with high density usage. Mobile source emissions from automobiles and stationary source emissions from manufacturing plants also become much more difficult to manage when they come from decentralized sources. Environmental noise problems are closely related to land use and population densities. Increasing solid waste generation from diverse sources raises the costs of collection and disposal systems by increasing transportation costs for solid waste, creating scarcities of nearby land for disposal, and limiting the number of options available to the solid waste manager.[1]

The following sections briefly describe the urban complex and the factors that relate increasing costs of urban environmental management to economic decentralization.

THE STRUCTURE OF URBAN COMPLEXES

Frequently, it has been observed that the large size and rapid growth of urban areas are responses to the income and employment opportunities they provide.[2] We can easily assume, based on this observation, that the conditions of production differ in critical respects between urban and non-urban areas and between urban areas of different size. It is also a common observation that the nature and intensity of land use vary greatly from city to city and from one part of a city to another.

Figure 1 is a schematic diagram that classifies urban activities into four sectors and depicts the rent gradient for each. (Rent gradient is the amount of money per unit of land that can be demanded at various distances from the center of the city.) Sector A in Figure 1 is nearest the city center and represents centrally located manufacturing and office activities. Sector B is the next nearest the center, representing low-income housing. Sector C represents suburban, high-income housing, and Sector D represents suburban manufacturing and office activities. In Figure 1, it is assumed that Sector D can pay more rent for suburban land than for central-city land, since intercity highway shipments of freight are cheaper from suburban locations than from central-city locations.

Cheaper land may induce a family to consume more living space at the expense of other items of consumption and with increased commuting

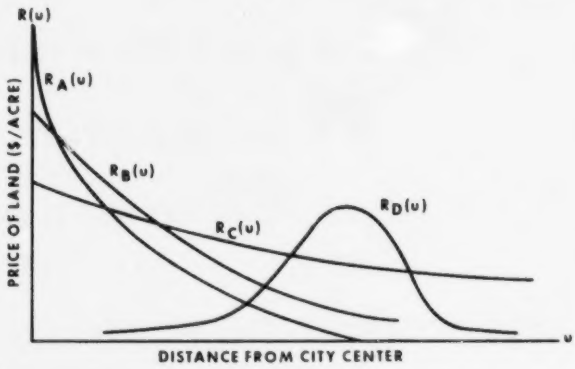

Figure 1. Theoretical analysis of urban structure.

dential districts, closer to their customers. These outlets require only a small client population, since per capita purchases are more frequent.

POPULATION DISPERSION AND THE COST OF ENVIRONMENTAL MANAGEMENT; A SOLID WASTE EXAMPLE

Mathematical models have been developed to describe the dispersion of population within and around urban areas. Several studies have provided strong evidence that population density falls off fairly smoothly and at a decreasing rate as one moves out from the center of the city.[3] time and costs. The choice of more space can be more readily exercised at high incomes than at low ones. Consequently, a model based on land value gradients will predict that more affluent families will live farther from the center of a city than will those of limited means. Businesses, too, will vary in their choice of location. Some small manufacturing industries and office activities require rapid access to each other, so they must choose central location over cheapness of space. Typically, offices are forced upward into skyscrapers as central space becomes more and more costly. On the other hand, some manufacturing industries need abundant land; and as the cost of land increases, they are led to move farther from the city. Major retail establishments where infrequent purchases are made by each buyer, have tended to seek central locations that would give the population of the entire city convenient access. The same pattern occurs with some cultural centers. Other more standardized retail and service activities have located in resi-

Figure 2 shows the tail end of the population density curves calculated for a large midwestern community. It is easy to see that the beginning of the area, designated as having a rural population density, is moving away from the center of the city. If we assume a rural population density of 250 persons per square mile, we can see that this frontier has moved from approximately 6-1/2 miles in 1948 to about 11 miles in 1970. As an example of the impact of population dispersion, we might examine its effect on available land for solid waste disposal. We can see that potential sites (as represented by low population densities) must be located farther and farther from the center of the city. Correspondingly, transportation costs for solid waste management must increase because of this spreading effect.

Given consumer preferences for low density living, and assuming that per capita income will continue to increase, it is reasonable to expect that this decentralization will continue and that the cost of maintaining a constant level of output for solid waste as well as other environmental management services will increase.

EFFECT OF LAND USE ON TECHNOLOGICAL CHOICE

Since convenient disposal sites will no longer be available close to the central city, it is logical to consider transfer systems to carry the waste away. Two types of transfer systems suggest themselves for consideration. One is the standard truck transfer system, whose technology and economics are well known, and the other is rail haul, which has been discussed a great deal but which has been studied only superficially.

Figure 3 summarizes the typical cost per ton for each of the two transfer systems in a large, midwestern city, including land disposal costs.

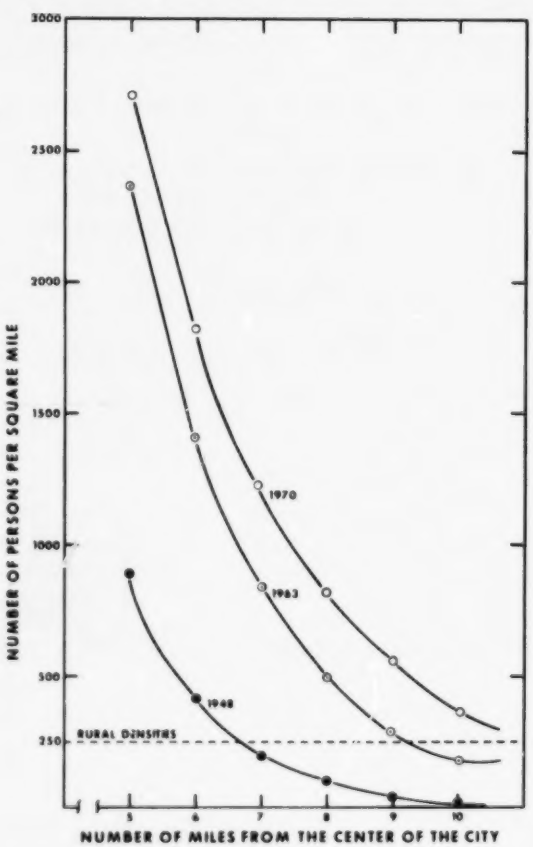

Figure 2. Tail of population density curves.

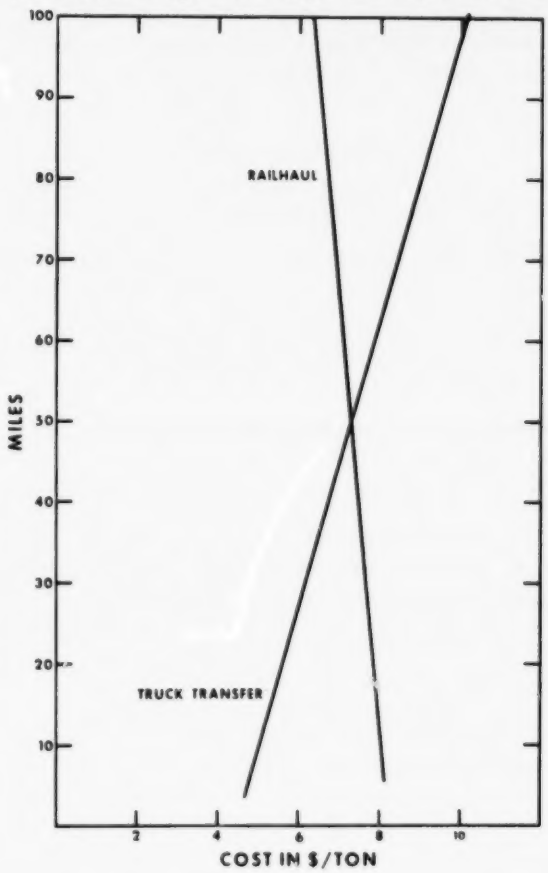

Figure 3. Total cost for rail haul and truck transfer.

At a 50-mile distance from the city, rail haul and truck transfer reach a break-even point at approximately $7 per ton. These data indicate that when population densities 50 miles distant from the city reach a level at which land disposal sites are no longer readily available, a new type of technology must be chosen for haul and disposal.

CONCLUSIONS

Relating land use and population dynamics to the choice of methods for solid waste disposal is only one example of how socio-economic variables can influence the choice of technology for environmental management. We are only beginning to understand these complex interrelationships, and much research remains to be done in this area if we are to avoid the crisis approach that has so often dominated the field of environmental management. More programs such as those being conducted at NERC-Cincinnati are needed to ensure that future research is well-planned and long-range in its approach.

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3. Mills, Edwin S. Studies in the Structure of the Urban Economy. In Resources for the Future. Baltimore and London, Johns Hopkins Press, 1972, p. 34-37.

Reports recently made available through the National Technical Information Service, Springfield, Virginia 22151, including the PB order number and cost:

"Municipal Waste Disposal by Shipborne Incineration and Sea Disposal of Residues," EPA-670/2-73-017, PB 221 684, cost $32.25.

"Study of the Economics of Hospital Solid Waste Systems," EPA-670/5-73-020, PB 221 681, cost $9.00.

"Incineration of Bulky Refuse Without Prior Shredding," EPA-670/2-73-023, PB 221 731, cost $3.00.

"A Recirculating Waste System for Swine Units," EPA-670/2-73-025, PB 221 621, cost $14.50.

"Radiolytic Hydrolysis of Cellulose," EPA-670/2-73-030, PB 221 877, cost $3.00.

"First Annual Progress Report on a Study of Corrosion in Municipal Incinerators," EPA-670/2-73-032, PB 221 851, cost $3.75.

"Wood Waste Reuse in Controlled Release Pesticides," EPA-670/2-73-034, PB 222 051, cost $4.85.

"Use of Domestic Waste Glass for Urban Paving," EPA-670/2-73-038, PB 222 052, cost $6.45.

"Pyrolysis of Solid Municipal Wastes," EPA-670/2-73-039, PB 222 015, cost $4.85.

"Mathematical Model for Post Aeration," EPA-670/2-73-044, PB 222 031, cost $3.75.

"A Mathematical Model for Aerobic Digestion," EPA-670/2-73-045, PB 222 029, cost $3.75.

"Design and Simulation of Equalization Basins," EPA-670/2-73-046, PB 222 000, cost $4.50.

"Hospital Solid Waste Disposal in Community Facilities," EPA-670/2-73-048, PB 222 018, cost $9.00.

"Combustion Products from the Incineration of Plastics," EPA-670/2-73-049, PB 222 001, cost $8.00.

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ANALYTICAL QUALITY CONTROL

September 14, 1973

OIL IDENTIFICATION: STATE OF THE ART

F. K. Kawahara and E. C. Julian*

BACKGROUND

Petroleum and its products enter the environment through accidental discharge of wastes, mistakes in the transfer of oil to and from tankers, shipwrecks, and the purging of cargo tanks by sea water treatment. The manufacturing or processing industry and the transportation industry are the main producers of oily wastes. Other sources are individually owned automobiles, boats, and airplanes. The deleterious effects of oil pollutants on the environment are well known – extensive damage to shorelines and beaches, destruction of marine life and the presence in water of toxic agents, noxious odors, and tastes.

As industrial activity continues to expand, the problem of both chronic oil pollution and large, catastrophic spills will occur more and more frequently. Thus, the ability to identify and characterize spilled oil samples in order to determine their source is becoming extremely important. The task is quite difficult, however, since samples are often highly complex mixtures containing several petroleum products. Severe weathering further complicates the matter by superimposing composition and chemical changes to the samples.

Measuring the concentrations of various components and physical and chemical properties of these samples has been the major approach to identification. Such an approach will include the measurements of major components, minor components, trace elements, spectral properties, and physical properties. A final identification step may involve data treatment and the use of statistical methods in data analysis.

*Both Dr. Kawahara (Group Leader, 513-684-2939) and Mr. Julian (Research Chemist, 513-684-2985) are with the Oil Identification group of the Analytical Quality Control Laboratory.

STATE OF THE ART

Sampling Considerations and Treatment. Oil samples collected from the environment may possess a number of disadvantages. A sample may contain large amounts of water and debris, it may be rather small, and it may have been weathered for some time before collection. Almost all methods will require that the sample be separated from the debris and water before applying any test. All samples, reference and spilled, should be subjected to distillation to 280°C in order to attain uniformity of composition of nonvolatiles.[21]

Physical Bulk Properties. Physical bulk properties such as asphaltene content, wax content, the congealing point of the wax, and specific gravity should be determined, if possible. These methods, together with others, have been reviewed.[9,21]

Chemical Bulk Properties. Chemical bulk properties may serve as a method of sample screening. For example, sulfur and nitrogen analyses are particularly helpful. Two methods, the oxygen flask technique and x-ray fluorescence analysis technique, may be applied to the determination of sulfur. The nitrogen content may be determined by a micro-Kjeldahl or microcoulometric technique. According to Brunnock et al.,[6] the sulfur content in crude oils shows a loss during weathering of about 15 percent. In spite of this loss, oil samples may be classified as "high sulfur" (more than 2% by weight), "medium sulfur" (1%-2% by weight), or "low sulfur" (less than 1% by weight). There is little information on the effects of weathering on nitrogen content.[32]

Spectral Properties. The use of infrared spectroscopy for petroleum identification has been described.[17,19] This method was used for the first identification and characterization case handled by the National Environmental Research Center, Cincinnati, Ohio. The situation involved the large, heavy, residual fuel oil and asphalt

spill that extended 45 miles from Wilmette, Ill., to Gary, Ind., and that contaminated Lake Michigan waters and beaches during September and October 1967.

Samples of beach materials and of lake water were collected from the oil spill area, and the Analytical Quality Control Laboratory (AQCL) of NERC developed a rapid analytical method utilizing infrared spectroscopy to analyze these heavy petroleum products (for which the evaporative effects are negligible). The unknown samples were determined to be a mixture of asphalt and No. 6 fuel oil, and the mixture was coupled to source samples of an industrial asphalt and No. 6 fuel oil.

Mattson[23] proposed the internal reflection technique to improve the reproducibility of the infrared spectra. In our opinion the condition of his sample, the presence of water, and the variable geometry of the sand surfaces will prevent attainment of reproducible sample area, and thus the spectra would not be reproducible. This opinion is in contrast to Adlard's statement.[1] A study of the possibility of using infrared spectroscopy for the remote sensing and identification of waterborne oil slicks has been made.[24]

Freegarde et al.[10] and Thruston and Knight[29] have applied ultraviolet (uv) fluorescence spectroscopy to identify pollutants. Freegarde[10] dissolved the cleaned-up sample in cyclohexane, subjected the solution to uv excitation at different wavelengths and obtained emission fluorescence spectra. Thruston and Knight[29] added three levels of sample concentration to the previous system. By this procedure, four pollutant samples were shown to have the same origin, with confirmation by elemental and infrared ratio analyses.

Mass spectrometry has been widely used for determining components in petroleum fractions since the molecular weight of the injected material is provided if the parent ion appears. The coupling of the gas chromatograph with the mass spectrometer has been especially helpful.[13] A review of published work on this coupling is available.[31] An application of the use of a high-resolution mass spectrometer for the group analysis of complex, unfractionated petroleum distillates was published by Gallegos et al.[12] The use of these high resolution measurements also makes it possible to estimate the contents of paraffins, monocycloparaffins, dicycloparaffins, etc., in a series of petroleum fractions, and to distinguish the types of aromatic and heterocyclic compounds present.

Component Separation Techniques. A number of component separation techniques based on chromatography have contributed to the identification of oily pollutants. Work done by Shuldiner in 1951,[28] paper chromatography followed by inspection of the chromatogram under uv light, is relevant today and applies to current problems.[15,22]

The use of column absorption chromatography was illustrated by Rosen and Middleton[27] who used silica gel columns for separating pollutants into fractions that were then examined by infrared spectroscopy.

Another chromatographic technique, gel permeation chromatography, has been applied to the fractionation of asphalt constituents. Altgelt[3] fully describes the preparation of the gel, column design, and sample preparation. One major peak is noted.

Another technique termed radial chromatography[14] has shown merit in comparing petroleum products. This technique combines capillary analysis and circular chromatography.

Gas-liquid chromatography (GLC), often used with high resolution and temperature programming, is a common method for separating materials into their components.[2,21] In a case of beach pollution[26] or oil leaks,[7] identification of petroleum sources illustrated applications of GLC for liquids at ambient temperature.

"Dual fingerprints" of the materials being studied may be obtained with chromatograph using dual detectors.[2,16] Brunnock et al.[6] used the n-paraffin components of crude oils as a kind of fingerprint for identification. GLC can also produce a simulated distillation pattern by means of an ASTM procedure.[4] The hydrocarbons C_{20} through C_{35} show typical distributions as related to various specific crude oil sources. With straight run No. 1 and No. 2 fuel oils, components are so similar qualitatively and quantitatively that identification by measuring n-paraffins is not useful for enforcement purposes.

Many chemical elements at trace levels[5] are contained in all crude oils and fuel oils. Because vanadium and nickel are present in the majority of crude oils and show considerable differences from one oil to another, both elements have been used as identification guides. The necessity for ashing the sample before the determination can lead to losses of these elements and may cause uncertain inferences. Several methods such as atomic absorption, x-ray fluorescence, emission spectroscopy and neutron activation vary in advantages and disadvantages. Adlard[1] considers the multitrace element technique the most definitive single method for identifying pollutant samples because the large number of parameters should produce characteristic correlations unique to the reference samples. Also, since these trace elements are found in the high boiling part of the oil, weathering should not have any effect on the ratios of these elements; but this is not always true as all trace elements are not bound in the stable form as chelates of porphyrin.

AQCL has developed a new and powerful method[18] to identify lube oils and asphalts. It is based on preparing certain volatile derivatives of weak acids and

mercaptans present in the samples and analyzing them by GLC with an electron capture detector. The method results in distinctive and characteristic patterns in the chromatograms of the heavier, non-volatile lube oils and asphalts. This is the first successful application of gas chromatography to analyses of heavy lube oils and asphaltic materials.

Techniques of Data Treatment and Mathematical Statistics. It has often been desirable to transform raw data before any analysis of the data is performed.[32] As an example, the use of ratios of absorbance in infrared spectroscopy offsets the effects produced by variation in sample film thickness.[30,17]

Using the technique of multivariate statistical analysis, all of the random variables may be analyzed simultaneously through the use of large computer systems and their attendant statistical packages.[6] At AQCL, the technique of data transformation and linear discriminant function analysis has been applied to infrared absorbance ratios.[20] As a result, asphalts and No. 6 fuel oils have been correctly classified with an average probability over both groups of 0.999. When a high probability is attained for the true classification of many samples from many groups, the potential of the multivariate procedure for identification of oil spills is recognized.

WHAT IS NEEDED

Much research needs to be done in the area of characterization and identification of highly complex mixtures containing several petroleum products. Examinations of simple mixtures of products of diverse physical and chemical properties, such as light gasoline and heavy asphalt, have usually resulted in identity and characterization when preceded by resolution to the individual products. However, a mixture of two similar petroleum products (asphalt and another asphalt, for example) presents unusual difficulty. Since products of companies have somewhat similar properties, advanced statistical analyses of multi-instrumental techniques will be necessary in correlating the maze of data parameters for obtaining maximum information.

Efforts should be directed toward studies of the long-term effects of crude oils, petroleum products, and oily effluents on the ecology. After the wreck of the Torrey Canyon (1967), Freegarde[11] detected in 1969 an accumulation of hydrocarbons in plankton obtained from the English Channel. There is danger that spilled oil may result in a buildup of polynuclear hydrocarbons in marine food-chains. Fish, marine mammals, and sea birds may eventually accumulate these hydrocarbons and other synergistic materials on a long-term basis. Thus, suitable studies are needed to differentiate mineral (fossil) oils from the biogenic oils. Some work has been initiated in this area.

Recent findings by Thor Heyerdahl and the U.S. Research Ship Atlantic II show that Atlantic and Mediterranean areas are polluted by oil globules and monomolecular oil film. Ottway[25] discloses that the amount of light absorbed by this oceanic pollution would have a noticeable effect on photosynthesis and would on a long-term basis, affect the atmospheric gas balance. Thus, studies should be conducted on the physical and chemical effects of oils – the rates of gas diffusion through oil films of varying types and thicknesses, for example.

The chemical, toxicological, and biological fate of crude oils and products is also an area for more research. The duration of the oil spill (as indicated by products of autooxidation and by ratios of certain elements) and losses from evaporation and solubilization should be studied in detail and depth with a great variety of petroleum product fractions. Aged samples in fresh and salt water, in ground and runoff water, and in swamp water probably vary widely in composition after exposure, even though the temperature, light, rate of evaporation, etc., are held constant.

A number of promising and effective methods of oil identification have been made available, as shown by the present state of the art. However, the great complexity produced by multiple oil spills and the covering of old oil spills with new ones will require even more sophisticated and effective means of identification. In addition, the toxicity problems will provide subjects to study for a long time to come.

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ADVANCED WASTE TREATMENT

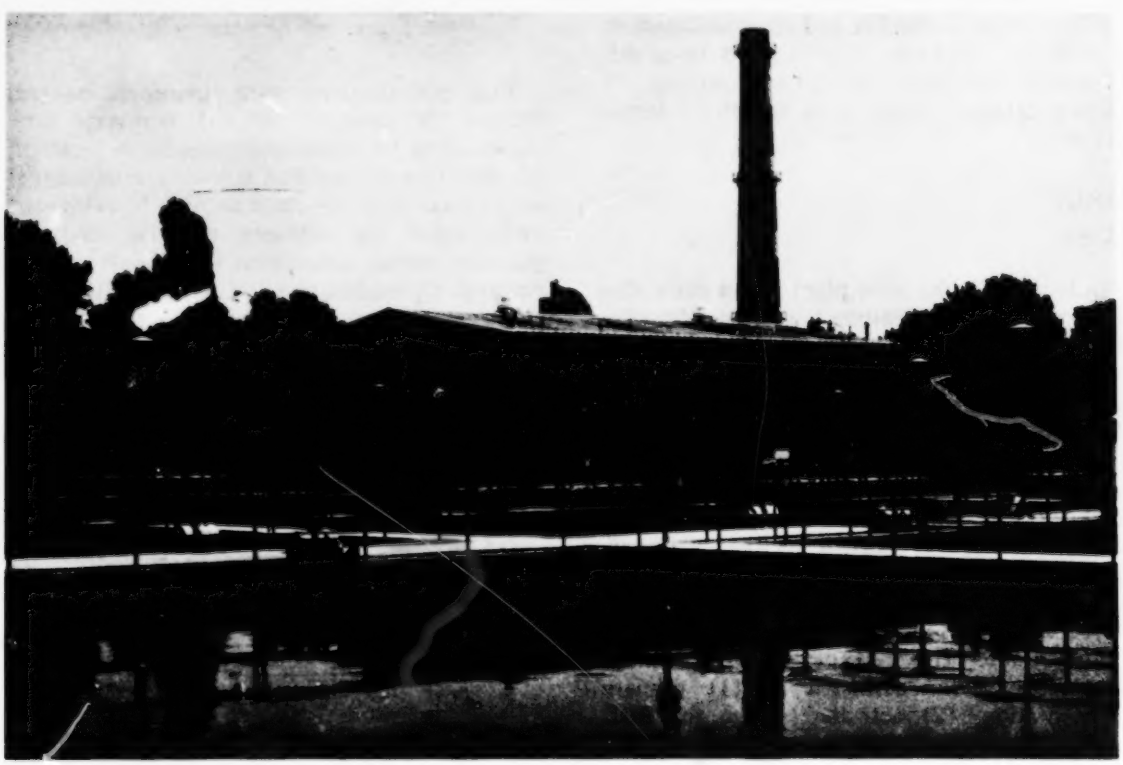
September 28, 1973

THE EPA–DC PILOT PLANT FOR WATER POLLUTION CONTROL

D. F. Bishop and J. M. Smith*

BACKGROUND

The EPA-DC Pilot Plant, located at the District of Columbia's Water Pollution Control Plant, was conceived in 1965 as a pilot facility for tertiary treatment of the District of Columbia's secondary effluent. Since the pilot plant began operation in 1967, additional pilot facilities (usually for a 50,000 to 100,000 gpd flow with various diurnal flow patterns) have been constructed to permit process evaluation



and to produce engineering design data for more conventional and waste treatment processes, including solids handling and disposal processes. The work evolved into studies of treatment systems composed of various combinations of processes, with two basic treatment approaches: physical-chemical and advanced biological treatment. Unlike early work in advanced waste treatment, the overall goal of the pilot facility was to evaluate complete treatment systems with associated solids handling for year-round removal of carbon (C), phosphorus (P), and nitrogen (N) and to develop engineering design data for constructing these treatment systems.

In 1968, the Potomac Enforcement Conference established vigorous standards for total pollutants in effluents discharged into the Potomac River. At projected 1982 flows, the allowable concentrations of pollutants for the Washington, D.C., plant discharge were 4.5 mg/l of BOD, 0.22 mg/l of P, and 2.5 mg/l of total N, respectively.

With the establishment of these standards, two immediate specific goals were assigned to the pilot plant: first, to develop and evaluate on a pilot scale various treatment systems to permit the District of Columbia and its consultants to select a system for its 309-mgd, advanced-treatment plant, and second, to develop detailed design data for the selected system.

EARLY WORK

In late 1969, the pilot plant began evaluating several parallel treatment systems for the District of Columbia: three-stage, activated-sludge treatment (Figure 1), physical-chemical treatment of raw wastewater (Figure 2), and conventional tertiary treatment (Figure 3). Pure-oxygen-activated sludge for BOD removal was studied as an alternate to the first stage (air-activated sludge) in the three-stage, activated-sludge process. Conventional tertiary treatment with mineral addition (Figure 4) was also studied on a small pilot scale.

The basic three-stage, activated-sludge treatment system consisted of (1) primary sedimentation, (2) activated sludge for BOD removal, and (3) nitrification and denitrification for nitrogen removal, with filtration of the final effluent for residual solids removal. Two alternates were evaluated for phosphorus removal. The first was separate lime precipitation on the denitrification effluent, and the second was mineral addition within the first and third activated-sludge processes. Step aeration, pure oxygen, and modified, activated sludge were considered as unit processes for carbonaceous BOD removal. Evaluation of the processes in the pilot plant revealed that modified aeration (the present District system) was most compatible with the complete treatment system.

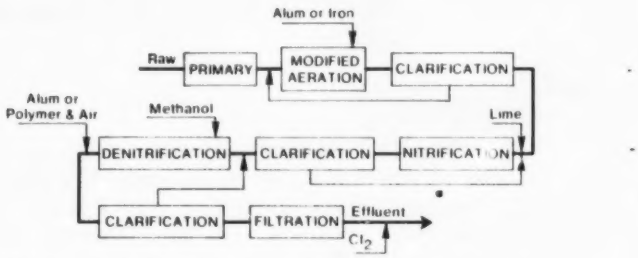


Figure 1. Three-stage, activated-sludge treatment.

The physical-chemical treatment system (Figure 2) consisted of (1) two-stage lime clarification for solids and phosphorus removal, (2) filtration for residual turbidity removal, (3) selective ion exchange or breakpoint chlorination for nitrogen removal, and (4) granular carbon adsorption for soluble organic removal. Ozonation was tested intermittently to remove residual organics from the carbon effluent.

The conventional tertiary treatment (Figure 3) consisted of (1) primary treatment and step aeration for solids and BOD removal, (2)

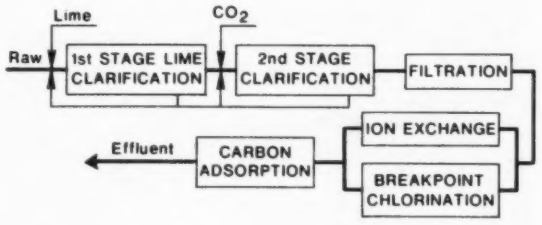


Figure 2. Physical-chemical treatment.

two-stage lime clarification for phosphorus removal, and (3) filtration of turbidity removal. Breakpoint chlorination and ammonia stripping were intermittently evaluated in the system for nitrogen removal. Selective ion exchange tested in the physical-chemical system could also be applied to the conventional tertiary system. In earlier work, carbon adsorption for removal of residual organics had been evaluated on chemically clarified secondary wastewater in the District of Columbia and was thus only tested on a small pilot scale.

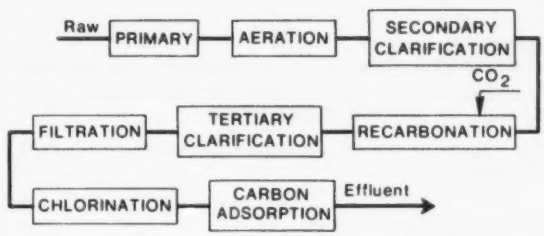


Figure 3. Conventional tertiary treatment.

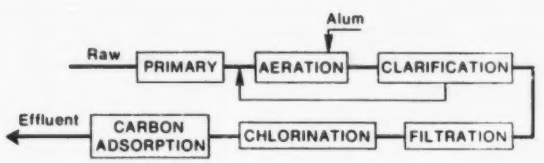


Figure 4. Conventional tertiary treatment with mineral addition.

Though the early studies indicated that each of the evaluated systems had the potential for meeting the discharge standard, the District of Columbia selected the three-stage, activated-sludge system with mineral addition as the most economical and the most compatible with the existing District facilities. The EPA-DC Pilot Plant then began and is now continuing to develop the detailed design data for the advanced wastewater treatment plant that is planned for the District of Columbia. Research and development for national application continues on various alternatives for physical-chemical treatment (including automation of the system with both analog and digital control systems) and on systems consisting of physical-chemical lime clarification followed by nitrification-denitrification (Figure 5). Work also continues on oxygen-activated-sludge treatment, including separate nitrification with pure oxygen.

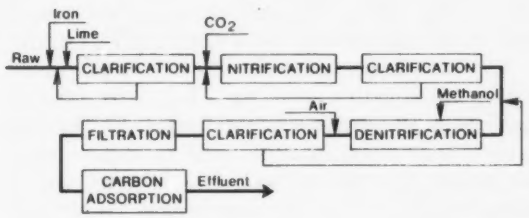


Figure 5. Lime-clarification, nitrificatio denitrification treatment.

THE THREE-STAGE, ACTIVATED-SLUDGE SYSTEM

The process design data developed for the District of Columbia's three-stage, activated-sludge treatment system (with mineral addition) include the following:

- chemical requirements (alum, $FeCl_3$, lime methanol)
- the BOD removal rates and the kinetics of nitrification and denitrification for sizing the biological reactors
- the settling and thickening characteristics and solids production for design of clarifiers and sludge wasting and recycle systems
- the sludge handling characteristics.

Work is currently under way to automate this sophisticated biochemical system.

The most important system design and process interactions are briefly described below. The first activated-sludge stage, with 2.5 hr of detention time, is operated with 1,100 to 1,800 mg/l of mixed liquor solids to provide a controlled BOD of 15 to 35 mg/l to the subsequent nitrification process. A residual BOD is required for reasonable bioflocculation in the nitrification stage. Control of the BOD residual is necessary because NH_3 breakthroughs occur if the

BOD entering nitrification exceeds 35 during the winter, especially during peak hydraulic flows. In the first stage, alum or $FeCl_3$ is required at a mole ratio of approximately 1.1 to 1 Al (or Fe to P) to insolubilize most of the phosphorus.

In the second activated-sludge process (nitrification), the pH of the influent is adjusted with lime (CaO) to produce an effluent pH of about 7. The lime neutralizes the nitric acid produced during nitrification and thus helps to provide maximum nitrification kinetic rates. The kinetic rates for nitrification during the winter determine the reactor size. For District wastewater with a 2:1 average-to-peak flow and approximately 2,500 mg/l of MLSS, the detention time in the reactor is approximately 4 hr for an average flow at a minimum water temperature of 55 F.

In the third stage (denitrification), methanol is added at about 175 percent of the stoichiometric requirement to serve as a carbon source in the anaerobic reactor. The anaerobic reactions reduce the nitrate to N_2. The winter denitrification kinetic rates in Washington require a 4-hr reactor similar to the nitrification reactor. A 30-min aeration stage immediately after the denitrification reactor and before the denitrification settler serves three functions: to remove nitrogen gas from the mixed liquor to improve sedimentation, to aerobically remove excess methanol, and to serve as a mixer during the addition of alum to precipitate residual phosphorus. The second alum addition increases the total Al:P dosage ratio to about 1.7:1.

The settlers for modified aeration with mineral addition and nitrification have conservative detention times of 3 hr. The settler for denitrification has a detention time of 2.5 hr.

The three-stage, activated-sludge system with mineral addition provides very reliable water qualities (Table 1). The residuals of BOD, COD, P, and N in all the effluents are averages of data from 10 months of continuous operation. The addition of carbon adsorption, although not required for the discharge standard, reduces the residual COD to 5 mg/l and thus produces final effluent qualities of 5 mg/l of COD, 0.15 mg/l of P, and 1.4 mg/l of N. With respect to carbon, phosphorus, and nitrogen, the residual pollutant concentrations are similar to those present before the water was used.

TABLE 1. EFFLUENT QUALITIES OF THREE-STAGE, ACTIVATED-SLUDGE TREATMENT

Type of effluent	Effluent quality (mg/l)*			
	BOD	COD	Total P	Total N
Primary	99.2	23.1	6.8	23.6
Aeration	23.6	64.3	1.5	16.7
Nitrified	15.9	22.4	0.87	13.5
Denitrified	9.0	26.7	0.46	2.1
Filtered	2.7	15.9	0.15	1.4
Adsorbed	—	5†	—	—

*Effluent qualities through the filtered stage are averages of data from 10 months of continuous operation.

†The effluent quality after adsorption represents typical COD after laboratory tests.

RESEARCH RESULTS OF OTHER SYSTEMS

Each of the remaining treatment systems effectively remove carbon, phosphorus, and nitrogen from the wastewater. The physical-chemical system produces the intermediate and the excellent final water qualities (Table 2). The residuals of BOD, COD, and P in all the physical-chemical effluents are averages of data from 10 months of continuous operation (but not always with a nitrogen removal process). The nitrogen residuals represent typical operation of the physical-chemical system with breakpoint chlorination or with selective ion

TABLE 2. EFFLUENT QUALITIES OF PHYSICAL-CHEMICAL TREATMENT

Types of effluent	Effluent quality (mg/l)*				
	BOD	COD	Total P	Cl_2	Total N Ion exchange†
Raw	129	307	8.4	22	23
Clarified	24	55	0.27	15	17
Filtered	20	49	0.18	14	16
N Removal	—	—	—	2.6	3
Adsorbed	6	15	0.13	2.5	2

*Effluent qualities for BOD, COD, and Total P are averages of data from 10 months of continuous operation.

†Effluent removals for N represent typical efficient operating performance for continuous operation.

exchange. Ozonation of the carbon effluent in laboratory and intermittent pilot tests indicated about 60 to 70 percent removal of the COD from the carbon effluent. Thus, using the physical-chemical system on District wastewater has produced excellent final effluent qualities of 5 mg/l of COD, 0.13 mg/l of P, and 2.5 mg/l of total N.

The effluent qualities (Table 3) for BOD, COD, and P in conventional tertiary treatment also represent averages of data from 10 months of continuous operation. Nitrogen removals and the effluent qualities after chlorination and adsorption represent typical operation during short pilot tests. The nitrogen removals require a complex control system for the breakpoint chlorination process but are basically independent of seasonal and wastewater variations, except for ammonia content. The final effluent quality of 7 mg/l of COD, 0.14 mg/l of total P, and 2 mg/l of total N represent very good water quality.

TABLE 3. EFFLUENT QUALITIES OF CONVENTIONAL TERTIARY TREATMENT

Type of effluent	Effluent quality (mg/l)*			
	BOD	COD	Total P	Total N
Raw	129	307	8.4	22
Secondary	19.7	59	6.7	17
Clarified	4.2	22.7	0.34	15
Filtered	3.3	21.7	0.14	14
Chlorinated	—	—	0.14	2
Adsorbed	—	7	—	—

*For BOD, COD, and P, effluent qualities through the filtered stage are averages of data from 10 months of continuous operation. Nitrogen removals and carbon adsorption effluents represent typical results of short pilot tests.

The lime-precipitation, nitrification-denitrification system has been operated with both single-stage and two-stage lime clarification. All effluent qualities (Table 4) represent typical operation of the system with single-stage lime precipitation. Final phosphorus removal by mineral addition and filtration of the denitrification effluent were not demonstrated in the pilot plant. The moderately high COD in the denitrification effluent represents a small overdose of methanol; however, correction of the methanol overdose and the addition of alum during denitrification, followed by filtration and carbon adsorption, should easily produce a final water quality similar to that demonstrated in the three-stage, activated-sludge system (Table 1).

TABLE 4. EFFLUENT QUALITIES OF LIME-PRECIPITATION, NITRIFICATION-DENITRIFICATION TREATMENT

Type of effluent	Effluent quality (mg/l)*			
	BOD	COD	Total P	Total N
Raw	100	251	6.2	21.8
Clarified	30	66	1.3	16.7
Nitrified	15	26	1.2	15.9
Denitrified	18	42	0.7	1.9

*Effluent qualities are averages of data from a typical month of continuous operation. Mineral addition, filtration, and adsorption were not employed in the sequence. The performance of these processes after denitrification would produce results similar to the three-stage, activated-sludge system in Table 1.

The effluent qualities given for the conventional tertiary treatment system with mineral addition (Table 5) are composites of typical effluent qualities from several pilot plant studies. Although the complete treatment sequence was not tested at the same time in the pilot plant, the system is a combination of well-documented, reliable pilot plant processes, and the complete effluent qualities represent a reasonable typical system performance. Thus, the final effluent quality of at least 8 mg/l of COD, 0.6 mg/l of total P, and 2 mg/l of total N for the District of Columbia's wastewater is possible.

TABLE 5. EFFLUENT QUALITIES OF CONVENTIONAL TERTIARY TREATMENT WITH MINERAL ADDITION

Type of effluent	Effluent quality (mg/l)*			
	BOD	COD	Total P	Total N
Primary	134	258	8.4	20
Secondary	12.0	47	1.8	15
Filtered	5	27	0.6	14
Chlorinated	—	—	0.6	2
Adsorbed	—	8	0.6	2

*The complete sequence was not tested at the same time. Component processes such as primary-secondary-filtered were all evaluated in the pilot plant, but at different times. The effluent qualities are composites from typical pilot plant tests.

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RADIOCHEMISTRY AND NUCLEAR ENGINEERING

October 12, 1973

MONITORING RADIONUCLIDES IN REACTOR EFFLUENTS

Herman L. Krieger and Bernd Kahn*

BACKGROUND

To satisfy increasing consumer demand, the power industry has rapidly expanded its means of generating electrical power from nuclear fuels. The number of full-scale, commercial nuclear power stations in operation increased from 2 in 1960 to 8 in 1970. At present, 25 such stations are in operation, and an additional 150 are being built or are on order. The Atomic Energy Commission (AEC) is responsible for regulating the industry. Their jurisdiction includes control over the discharge of radioactive effluents and the emission of direct radiation that may lead to exposure of the general population. The U.S. Environmental Protection Agency (EPA) is, in turn, responsible for formulating the applied radiation protection standards.

Exposure of the population to radiation from operating nuclear power stations is very low when compared with either Federal Radiation Council (now EPA) guidelines or the natural radiation background to which everyone is exposed. Moreover, direct exposure in the vicinity of the stations applies to relatively few persons, and the contribution of the stations to worldwide radioactivity has been very small.[1] This problem area differs from many other EPA concerns in that the main effort now is to maintain environmental quality rather than to reduce serious pollution.

Keeping the public informed on radiation matters is unusually important because of the high level of awareness and concern. This deep public concern is attested to by frequent newspaper and magazine articles, the attention paid to speakers who paint alarming pictures of nuclear hazards, the number of interveners in hearings to issue building and operating permits, and the law suits filed to prevent the operation of nuclear power stations.

At the National Environmental Research Center - Cincinnati (NERC), the Radiochemistry and Nuclear Engineering Laboratory has undertaken studies to provide factual information on the extent of radiation exposure at nuclear power stations. The specific program of measurements is intended to (1) identify and quantify the radioactivity and direct radiation from typical stations, (2) delineate the main pathways leading to exposure of the population to radiation from these sources, (3) indicate the magnitude of radiation exposure to the population, and (4) present effective monitoring procedures. This program is supported by both the Office of Radiation Programs and the Office of Research and Development.

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STATE OF THE ART

Radiological surveillance around nuclear power stations presents difficulties because of the following factors:

- the complexities of station operation, waste treatment, and waste discharge patterns;
- the multitude of radionuclides produced and discharged;
- the differences in radiations, half-lives, and radioactivity levels that must be detected;
- the complex effects of the environment on the pathways, transfer coefficients, dispersion, and radiation exposures; and
- the extremely low levels of radiation and radionuclides.

Information concerning each power station and its immediate environment is available in environmental statements, safety analysis reports, and the annual radionuclide discharge reports that are submitted to the AEC. General guidance on environmental surveillance has been provided by several national and international agencies concerned with radiation protection. Specific programs and analytical methods may be patterned on those used by nuclear research laboratories, but some aspects of radiological monitoring must be developed specifically for nuclear power stations. These stations usually have only a small staff for radiological monitoring, are not distant from population centers, and discharge distinctly different mixtures of radionuclides. Particular analytical problems arise because (1) so many radionuclides of surveillance interest are present in effluents, (2) extremely low levels of radioactivity must be measured in environmental media, and (3) diverse substrates are encountered in environmental samples.

RADIOCHEMICAL ANALYTICAL METHODS FOR QUALITY ASSURANCE

In the period 1968-73, the Radiochemistry and Nuclear Engineering Laboratory undertook four field studies in the vicinities of operating commercial nuclear power stations. Radiochemical procedures were developed and improved in connection with these field studies. The studies served a two-fold purpose: providing the variety of samples needed to indicate the radionuclides of interest and to test the methods, and identifying and quantifying the radionuclides at the stations and in their effluents.[2,3]

Nuclear stations with a sufficiently long operating history and a variety of desired environmental parameters were selected for study. Both kinds of U.S. power reactors – boiling water and pressurized water – were studied. Sampling occurred during different periods in the operating cycle (including full-power and refueling) to evaluate the known variety of source terms. The stations, located on plains, in valleys, and on the sea coast, also provided the variety needed to consider dispersion and transfer of radionuclides in the environment.

The methods were developed for recommendation by EPA to assure the quality of data on environmental radioactivity. They are available for use by utilities, state agencies, and EPA monitoring networks. The methods include purely instrumental procedures such as gamma-ray and alpha-particle spectrometry, radiochemical procedures for separating and counting radionuclides, concentration and physical separation techniques to distinguish various forms of the radionuclides.

Over the period of study at the nuclear power stations, a wide range of wastes was sampled and analyzed. When samples were taken from within the reactor system to determine the nuclides in the highest concentration, only a few milliliters were needed for analysis. Other samples collected in air or receiving waters at varying distances from the plant discharge to corroborate dilution factors required 1 to 100 liters for analysis. Samples of soil, vegetation, algae, fish, meat, milk, and precipitation were also collected for analysis. Thus, the radionuclide composition of these media ranged from mixtures of many radionuclides in the microcurie-per-milliliter range to barely detectable levels lower in concentration by 10 orders of magnitude.

From the results of each field study, the radionuclides of surveillance interest could be identified. These included the major fission and activation products, such as ^{3}H, ^{14}C, ^{51}Cr, ^{54}Mn, ^{58}Co, ^{60}Co, ^{85}Kr, ^{89}Sr, ^{90}Sr, ^{131}I, ^{133}Xe, ^{134}Cs, and ^{137}Cs.

A laboratory manual consisting of 38 procedures for analyzing the nuclides in reactor aqueous solutions has been published as an EPA report.[4] When an analytical procedure was selected tentatively, it was employed on all subsequent samples. If the results of these radiochemical separations gave evidence of unsatisfactory purification, the method was modified or replaced. The methods finally selected were tested in a cooperative program with the NERC-Research Triangle Park group at the Montgomery, Alabama, laboratory. The methods underwent replicate testing with reactor coolants, reactor wastes, and specific tracer solutions. The criteria established for each method were: chemical yields greater than 70 percent, decontamination factors of at least 10^3, procedure time commensurate with the half-life of the nuclide being separated, and ease of analysis.

The system followed for analyzing each radionuclide consists generally of adding a standardized carrier to the test solution to give about 20 mg as the final precipitate and stirring to effect complete interchange between the stable and radioactive components in the solution. Two of the procedures (those for neptunium and technetium) require nonisotopic carriers for yield determinations, since standardized carriers are not available. For samples containing nuclides in several oxidation states, complete interchange with the stable carrier requires strong oxidative and/or reductive treatment during the initial steps of the procedures.

After concentrating the sample and purifying the nuclide by precipitation, evaporation, ion exchange, solvent extraction, or distillation, the final precipitate is collected on a glass-fiber filter and counted with the appropriate radiation detector. Identification of the radionuclide is confirmed by ingrowth/decay measurements, gamma-ray peak identification, and beta-particle absorption determinations. When required, repeated spectral analyses and decay measurements were made to identify and quantify isotopes of the separated radionuclides (for example, ^{134}Cs, ^{136}Cs, and ^{137}Cs). The method capabilities and decontamination factors were determined for each procedure after replicate tests.

In the course of repetitive radiochemical analyses of reactor discharges, several problems were observed. These included incomplete purification (decontamination) of specific radionuclides in coolant water and reactor wastes, incomplete carrier-radionuclide exchange, loss of activity by adsorption on container or by volatility, and cross-contamination of separated fractions (particularly when very high- and low-level activity samples were analyzed simultaneously). Ultimately, the procedure to be selected and the modifications to be included are determined from experience. Activity loss on container walls, for example, is minimized but not eliminated by acidifying the sample at the source with concentrated HNO_3 (1 volume acid to 10 volumes solution) and by analyzing for all activities soon after collection. Radioiodine and carbon-14 analyses, however, are made on separated aliquots from an unacidified sample to prevent losing volatile fractions.

These procedures for analyzing reactor aqueous discharges are hopefully undergoing closer scrutiny now that the manual has been distributed. Future supplements will be compiled and distributed as conditions warrant.

RELATED DEVELOPMENTS

Concurrent with this methods development for analyzing reactor effluent, procedures for separating and quantifying the nuclides in reactor gas stack effluents are being developed. These include testing the use of (1) a noble gas separation apparatus built by NERC-Las Vegas for the quantitative separation of krypton-85, followed by scintillation counting and (2) a gas catalytic combustion system for separating various chemical forms of tritium and carbon-14 and preparing them for measurement.

Procedures for measuring selected radionuclides in sea water and in soil samples are also being tested and improved as needed. Although ion-exchange concentration techniques for determining radionuclides in river water are available and have been utilized,[5] sea water requires alternate techniques such as the use of inorganic exchangers and specific resins.

Also being considered are methods to identify the radionuclides discharged from fuel reprocessing plants and other types of nuclear power stations. Entirely different spectra of radionuclides are expected from these sources, and methods are to be tested in conjunction with studies around these facilities.

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"Preventing Landfill Leachate Contamination of Water," EPA-670/2-73-021, PB 222 468, cost $4.25.

"The Effect of Processing Poultry Manure on Disease Agents," EPA-670/2-73-041, PB 222 148, cost $4.00.

"Survival of Pathogens in Animal Manure Disposal," EPA-670/2-73-051, PB 222 337, cost $4.50.

"The Nitrite-Accelerated Photochemical Degradation of Cellulose as a Pretreatment for Microbiological Conversion to Protein," EPA-670/2-73-052, PB 222 115, cost $5.45.

"Problems and Opportunities in Management of Combustible Solid Wastes," EPA-670/2-73-056, PB 222 467, cost $9.75.

"A Study of Incinerator Residue Analysis of Water Soluble Components," EPA-670/2-73-057, PB 222 458, cost $3.75.

"Composted Municipal Refuse as a Soil Amendment," EPA-670/2-73-063, PB 222 422, cost $3.50.

"Economic and Technological Impediments to Recycling Obsolete Ferrous Solid Waste," EPA-670/5-73-021, PB 223 034, cost $3.50.

"Study of the Technical and Economic Feasibility of a Hydrogenation Process for Utilization of Waste Rubber," EPA-670/2-73-066, PB 222 694, cost $4.50.

Reports currently available from the Technical Information Office, NERC-Cincinnati:

"Environmental Research Publications," EPA-670/9-73-004. (list of NERC-Cincinnati reports)

"Annual Report, 1972," NERC-Cincinnati, EPA-670/9-73-055; also available from the National Technical Information Service as PB 222 910, cost $3.75.

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SOLID WASTE RESEARCH

October 31, 1973

USING RECLAIMED RUBBER TIRES IN ROAD DRESSINGS

Richard A. Carnes*

In 1969, almost 230 million new pneumatic tires of all kinds (including 197.7 million passenger car and truck tires) were shipped by domestic tire manufacturers in the United States;[1] an additional 14 million new tires were imported either as original equipment on imported cars or separately.[2] More than 46.5 million retreaded tires were sold the same year.[3] After their useful lives have expired, these tires are discarded at a rate reported by the Goodyear News Bureau (release number 14982-970, September 24, 1970, page 2) to be approximately 180 million per year.

Although they make up only a small fraction of our national solid waste management burden, tires are among its more intractable components. In the past, tires were dumped and burned in the same manner as other refuse. Whole tires burned with the augmented air supplies present in modern incinerators are troublesome not only because of their combustion by-products but because their concentrated, high, thermal content damages incinerator grates and refractories. In sanitary landfills, whole tires, incorporated in bulk, spring back to their former shape after compaction and tend to work their way to the surface during settling, finally emerging through the landfill surface. Tires are extraordinarily durable, biologically inert, and extremely slow to decompose.

Retreading is the most obvious and economically attractive form of tire recycling. It is, however, inherently incapable of becoming a final use for used tires, since each retreaded tire must ultimately be discarded. Retreading can be regarded as an end use to the extent that it reduces the amount of tire waste produced in any given period. In this sense, it is already significant, since without retreading there would be some 22 percent more passenger tires discarded per year. There is persuasive evidence that retreaded tires can perform as satisfactorily as new tires in nonpassenger tire use. Retreads make up some 37.5 percent of the tire sales in the truck and bus market, and the average tire for a truck or bus is retreaded 1.8 times, many four or five times.

The small amount of reclaimed rubber presently used in new tire production does not reflect a lack of economic incentives, but a lack of technological capability. There appears to be little prospect of improving this capability sufficiently to make recycling of reclaimed rubber an effective means of scrap tire disposal. The output of the reclaiming industry was lower in 1968 than in 1958 and was expected to decline further in the 1970's.[4] Increasing demands on automobile performance and road engineering suggest that this decline is not likely to be halted. Highway speeds are increasing by about one-half mile per hour per year, and reclaimed rubber is not well suited to tires intended to be operated at high speeds.[5] There are other products originating from reclaimed rubber, mostly of a noncritical nature such as elastic webbing, floor mats, sink mats, rubber hoses, etc., but these constitute a small portion of the overall market picture.

The reclaiming industry presently uses about 50 million tires per year, or 20 percent of the tires produced. Major inputs to this industry are rubber factory scrap, tire buffings, and inner tubes. Economic trends indicate a decreasing market for reclaimed rubber because several grades of virgin rubber are now underselling it. The cheaper virgin rubber would certainly be more desirable, since reclaimed rubber is usually only about 50 percent rubber polymer; the remainder is reclaimed oils.

Over the years, there has been considerable interest in "rubberized roads." The technical literature contains many papers describing the use of rubber with asphalt for constructing highways.[6] These papers presently discuss only two types of use. The most prevalent one is the blending of chopped-up tires with asphalt for use as a paving composition. The chopped tires replace a large portion or all of the aggregate (crushed rock or gravel) in the paving composition. Several State highway departments have explored this application and reported advantages such as decreased skidding, longer road life, and decreased cracking and spalling of the surface.

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The second mode of rubberizing roads described in the literature involves adding rubber latex (unvulcanized) to the hot-mix asphalt paving composition. The same advantages are claimed as for the previous procedure, but unfavorable economics and a lack of durability are noted.

Several valuable bibliographies on the use of rubber in roads have been prepared and are kept up to date.[7] A review of these bibliographies plus a thorough literature search fails to disclose a single reference to the emulsification of a dispersion of vulcanized rubber in either asphalt or coal tar for specific use as a blacktop dressing for coating driveways, parking lots, etc.[8] Thus, the Solid and Hazardous Waste Research Laboratory of NERC-Cincinnati has supported research directed toward such use.

PROCESS DEVELOPMENT

Scrap rubber tire samples were obtained from a variety of sources for the experimental phase of this project. The Rubber Reclaimers Association supplied samples of reclaimed rubber representing materials that could be made by any reclaimer; the Union Carbide Corporation supplied a sample of cryogenically ground whole tires; and the A. Baker Manufacturing Company supplied samples of ground passenger-car tires. The asphalt base used in this study, a petroleum residue asphalt with a penetration of 190, was obtained from the Ashland Chemical Company and represented their recommendation for water emulsion use. The coal-tar base, obtained from Reilly Tar and Chemical Corporation, is a standard emulsion-type base sold by the supplier to many blacktop-dressing manufacturers.

Incorporation

After several methods of incorporating the various types of rubber samples into asphalt and coal tar were investigated, the following two procedures were selected because of economics, ease of incorporation, and appearance of the mixture of rubber-asphalt and rubber-coal tar.

The first method, developed by the Battelle Institute, employed the Bramley mill, a modified sigma-blade mixer that places high shear and tearing action on thick mastic materials. The asphalt or coal tar was placed into a jacketed Bramley mill, and the ground rubber added during agitation. The best technique was to heat the mill to between 265 and 275 F with 45 to 50 psig steam after addition of the asphalt or coal tar. When the asphalt or coal tar was liquid, the rubber was added. After 1 hour, the steam was turned off, and for an additional hour, cold water (40 to 45 F) was circulated through the jacket. This cycle was repeated four times.

The Engineering Department of the City of Phoenix[9] developed the second process method and has applied for a patent. The process involves heating the asphalt to 350 F and adding 25 percent ground rubber (-16 mesh, +25 mesh) to the heated asphalt during agitation. Slightly higher temperatures (375 to 380 F) were necessary to combine the ground rubber into coal tar.

Emulsification

The asphalt and coal tar used during the incorporation studies were the same as those used for the emulsification development. The following formulations were used for exterior evaluation:

Asphalt. All emulsions were made on a laboratory-model Cowles Dissolver. The asphalt control material and the five experimental emulsions were formulated as follows:

1. To the dissolver tank were added:
   9 kg water
   3 kg Mistron ZCS talc (to achieve more stable emulsions)
   60 g calcium chloride
2. The mixture was heated to 160 F with constant agitation; 4.5 kg asphalt or asphalt-rubber mix was then added and heated to 200 to 210 F during constant agitation.

Coal Tar. The four experimental coal-tar and rubber emulsions and the control were formulated as follows:

1. To the dissolver tank were added:
   7.2 kg water
   1.2 kg Burgess #20 clay
   0.6 kg Mistron ZCS talc
   60 g Indulin W-1 (the emulsifying agent)
   60 g calcium chloride
2. The mixture was heated above 180 F with constant agitation, and 5.4 kg coal-tar and rubber mix was added.
3. The mixture was then heated to 220 to 230 F during constant agitation. Immediately after all the coal-tar and rubber mix was added, 60 g potassium ricinoleate was added. The potassium ricinoleate caused the globules to break up and resulted in a good emulsion.

The nine experimental and the two control emulsions were applied to an evaluation site that was near the entrance to a parking lot where an estimated minimum of 1,800 cars per day would pass over the experimental emulsions.

RESULTS

Most of the experimental emulsions were applied to the driveway with no difficulty. When application problems did arise, they resulted from emulsions containing the 25 percent level (upper test limits) of ground rubber. Several of the experimental emulsions were gray when dried, indicating that too much extender material (talc and clay) had been used in the formulation.

A special test device was used to determine the slip resistance of experimental emulsions brushed onto a

TABLE 1. WEATHER-O-METER EVALUATION OF EXPERIMENTAL EMULSIONS

Comp components	% Rubber	Method of rubber incorporation	1000-hr evaluation comments
Asphalt-Xylos lx	5	BCL	Smooth, very slightly checked, gray
Asphalt-Baker fine	5	BCL	Slightly checked, whitish, few rubber chunks
Asphalt-Union Carbide	5	BCL	Considerable checking, whitish, eroded
Asphalt-Baker fine	25	Phoenix	Rough, slight cracks, rubbery
Asphalt-Baker fine	5	Phoenix	Smooth, gray, very slightly checked
Coal tar-Xylos lx	5	BCL	Dull, heavily alligatored, pinholed
Coal tar-Union Carbide	5	BCL	Dull, very heavily alligatored, pinholed
Coal tar-Union Carbide	25	Phoenix	Slight surface cracks, whitish, pinholed
Coal tar-Baker fine	5	BCL	Extremely alligatored, pubby blisters
Coal tar-Control	0	Commercial	Bronzed, flat, pinholded, thin
Coal tar-Baker fine	25	Phoenix	Very rough, no checks, no pinholes
Coal tar-Union Carbide	5	Phoenix	Black, smooth, few pinholes
Asphalt-Union Carbide	25	Phoenix	Considerable checking, gray, thin, eroded

damp piece of 1/8-in. asbestos board. All of the experimental coal-tar and rubber emulsions had improved slip resistance, both wet and dry, when compared with the commercial control. Even greater slip resistance was noted with the experimental asphalt-rubber emulsions, except in one sample, where evaluation was impossible because of large chunks of rubber on the coating surface. It was postulated that the asphalt emulsions all showed greater skid resistance than the coal-tar emulsions because of the slightly softer films of asphalt (Table 1).

Both the Battelle and the Phoenix incorporation processes gave highly satisfactory results during the course of this experiment. Overall, very satisfactory durability and resistance to oil and gasoline were observed for the experimental samples exposed for 1 year. The controls showed appreciable wear and were in definite need of resurfacing after the observation period. Cracks in the driveway were noted before application and after the conclusion of the evaluations. All cracks remained sealed, either when coated by experimental emulsions or by controls.

CONCLUSIONS

The feasibility of incorporating ground rubber from discarded automobile tires in bitumens to prepare a product suitable for use as a blacktop dressing has been clearly demonstrated. The economics seem to be favorable, since it appears possible to improve the performance of asphalt to essentially match that of coal tar. The overall economics will, of course, depend on the optimum level of rubber in the bitumen.

Assuming that 10 percent rubber is the optimum concentration, each gallon of emulsion would contain approximately 1/2 lb of ground rubber. This gallon would normally cover about 40 sq ft. One passenger-car tire, after removal of the bead and the major part of the fabric, will yield approximately 10 lb of ground rubber, or enough to prepare 20 gal of emulsion. The average driveway is estimated to be about 800 sq ft and would require about 20 gal of dressing for good protection. About one tire per average driveway would therefore be used. In addition to driveways, the millions of square feet of blacktop in shopping center parking lots, city streets, airport loading aprons and taxi strips, etc., could furnish enough area to use virtually all passenger-car tires discarded each year.

FUTURE NEEDS

The topping materials tested in these exposure-evaluation studies represent only the starting point for developing formulations. Future developments should be directed toward (1) selecting optimum raw materials used for the emulsions; (2) establishing optimum rubber-bitumen ratios; (3) identifying the best preparation techniques; and (4) testing long-range stability. These studies have also revealed that there may be many uses for these rubber-bitumen blends other than blacktop dressings. These might include vehicle under coats, coatings for underground protection of steel structures (tanks, pipes, etc.), roofing (composition and built-up), marine paints, adhesives, acid-proofing (battery cases, etc.), waterproofing, expansion joints (concrete construction), sound and vibration dampeners, sealants, caulking compounds, paper impregnants, ammunition case enamels, and thermal insulation.

Throughout the course of these studies, considerable interest has been exhibited by both government agencies and industrial organizations. Further refined research, based on these very favorable observations, should be sponsored by interested industry and/or other government agencies experiencing a scrap rubber tire disposal problem. Follow-up studies and refinements could logically aid in solving a solid waste disposal problem and develop, at the same time, a salable product of improved quality and favorable economics.

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ADVANCED WASTE TREATMENT

November 9, 1973

CONSERVING WATER AT HOME

Harry E. Bostian*

Conservation of water can extend the reserves of our treated and natural water supplies and will obviously lower per capita costs of water supply and wastewater treatment. Where the reduction of sewage flow is important, reduction of infiltration is probably the best approach. However, when water supply is the problem, water conservation is the only way to reduce demand. This paper considers two aspects of user conservation: reducing the use of and recycling water in the home. In the discussion below, we will consider the incentives, report on the results of two recent studies, and project the direction future work may take.

WATER USAGE AND SAVINGS POTENTIAL

Percentages of total fresh water and publicly supplied water used for various purposes are shown in Table 1 and Figure 1, respectively. Although domestic water use is but a small percentage of total water use, it accounts for a fairly large percentage of the water obtained from public water supplies. Increase in the use of recycled industrial water will tend to raise the domestic use percentage even higher.

TABLE 1. TYPES OF WATER USE FROM FRESH WATER SUPPLIES[1]

Use Category	Percent
Public Water Supplies	9.6
Rural Domestic	0.9
Industrial	18.7
Power Generation	25.3
Agriculture	45.5

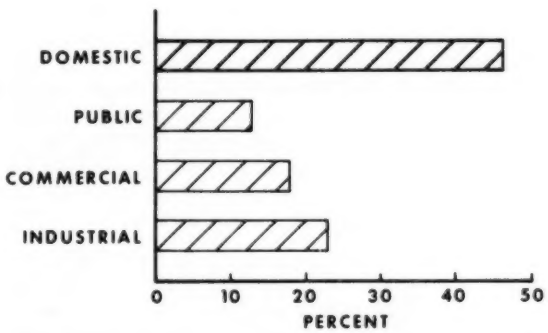

Figure 1. Use of water from public water supplies.[1]

The percentages of water used for various household purposes are given in Table 2. Most is used for toilet flushing, bathing, and laundering, and these three uses offer the highest potential for water savings.

There are already on the market several kinds of plumbing fixtures that require less water. Also, systems have been designed and tested that can recycle a portion of household water for uses not requiring drinking water quality. If all costs are considered, it may be cost effective to adopt some of these systems at the present time.

TABLE 2. HOUSEHOLD WATER USES[2]

Use Category	Percent
Toilet Flushing	27-45
Bathing	18-36
Laundering	18
Kitchen	13
Lavatory	4
Utility	2

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ELECTRIC BOAT'S FLOW REDUCTION AND WATER RECYCLE STUDY[3]

After the Electric Boat Division of General Dynamics identified potential areas for water saving,[4] they proposed a demonstration project. Early in 1971, EPA funded a contract for an eight-home demonstration that employed flow-reducing plumbing fixtures and recycle systems to reuse bath and laundry water for toilet flushing and lawn watering. The bath water used for recycle was from the tub drain. Lavatory water was not recycled. To obtain comparison data, the program was divided into 6 months of normal usage, followed by 12 months with water saving, and then another 6 months of normal usage after the water saving devices and recycle systems were removed.

Eight homes were involved: Electric Boat monitored six in the Groton, Connecticut, area; and the Convair Division of General Dynamics monitored two in San Diego, California, for Electric Boat. The available plumbing fixtures that were tested included shallow-trap toilets, flow-limiting shower heads, and two different kinds of dual-flush toilet modifications. The recycle systems combined filtration with chlorine disinfection. Not all the devices or concepts were used in all of the homes.

Details on the operating principles of the flow-reducing fixtures and the recycle systems may be of interest. The two flow-limiting shower heads, manufactured by Speakman,* restricted the flow to 2.5 and 3.5 gal/min, respectively, and employed flow-limiting orifices. The normal flow in conventional shower heads can be as high as 6 to 10 gal/min. The shallow-trap toilet, manufactured by American Standard, is effective with less water because the lip in the down leg of the trap is so designed that a solid plug of water is formed and initiates a seal quickly. A similar model is available from Crane, and a model is being developed by Kohler. Water Save, Inc., supplied a dual-flush device, the Econo-Flush, that modified existing toilets with plastic tanks that reserve a portion of the normal flush water. The plastic reserve tanks are inverted, open tanks that can hold water by vacuum when the outer flush tank level goes down. A light flush can be used for nonsolid waste; lifting up on the flush handle initiates a cycle that retains water in the reserve tanks. A full flush can be optioned by pushing down on the flush handle; this vents the reserve tanks, breaks the vacuum seal, and permits the reserve tanks, along with the remainder of the flush tank's volume, to empty. The Sink-Bob, supplied by Utah Marine, Inc., is another dual-flush device used in the study. It consists simply of a polystyrene float connected by a ring to a metal sinker. The device is fastened to the mechanism that closes the flush tank outlet. Depending on the placement of the Sink-Bob device, when the tank level goes down to a definite level during the flush, the float supporting the sinker lowers and the sinker weight causes the tank exit to close at a point before the tank is completely empty. If a full flush is desired, holding the handle down will override the Sink-Bob action.

Cost data on the flow-reducing devices is as follows. The cost of the shallow-trap toilet is not significantly different from conventional models. Flow-reducing shower heads cost 15-20 percent more than conventional models; however, this is a low cost item, under $10. The Econo-Flush dual-flush cycle modification is in limited production and is priced at $13.95. Its cost should be less if mass produced. The Sink-Bob is not presently on the market (Electric Boat obtained pre-production samples) but its retail cost, if it were manufactured, should be under $3.

For the recycle systems, no manufactured or prototype systems were available. Instead, they were assembled from components in a manner similar to constructing a small pilot plant. The systems consisted of a collection tank for bath tub and laundry water; a disinfectant feeder to disinfect the contents of the storage tank; a diatomaceous earth (Dia Clear, Inc.) or cartridge-type filter (FRAM and AMF Cuno with 5- to 25-micron elements), and a pump – pressure tank combination for supplying treated water for toilet flushing or lawn watering. For disinfection, an HTH tablet dispenser manufactured by Olin and an airlift Clorox feeder were used. All components could be made to perform satisfactorily; however, the diatomaceous earth filter had a longer on-stream time between servicing (backwashing) than the cartridge filter had between element changes, and would probably be preferred. Figure 2 is a schematic diagram of the arrangement in a home having a recycle system and a full complement of flow-reducing devices.

In Table 3 are summarized the water savings achieved during the period when the reduced-flow plumbing fixtures and recycle systems were installed. As might be expected, the wash-water recycle system showed the largest impact on water savings – an average of 27 percent reduction in total water usage. The dual-flush devices and shallow-trap toilet showed average savings in total water used ranging from 3.3 to 8.6 percent. The percent savings for the reduced-flow shower heads is quite low and is probably not statistically significant. The reason for this is believed to be the personal bathing habits of the individuals; many seemed to prefer tub baths to showers. In the WSSC study, discussed below, where a larger sample size was used, the reduced-flow shower head reportedly reduced water use more significantly.

A user survey conducted at the end of the Electric Boat study showed high acceptance for the flow-reducing devices. The acceptance percentages for flow-limiting shower heads, shallow-trap toilets, and dual-flush devices were 88, 83, and 100 percent, respectively. Somewhat lower acceptance was expressed for recycling:

*Mention of a commercial product does not constitute endorsement by the U. S. Government or by General Dynamics.

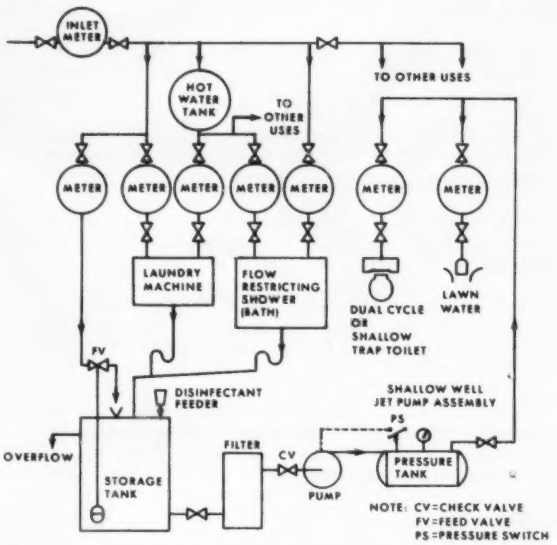

Figure 2. Schematic diagram for metered uses in homes with flow-restricting shower, dual-cycle or shallow-trap toilet, and washer-water recycle system. From the Electric Boat Study.[3]

TABLE 3. WATER SAVINGS SUMMARY[3]

Unit tested	No. of units tested	No. of occupants, avg.	% reduction total water use
Wash water recycle system	3	6.3	27.0
Shallow-trap toilet	6	4.5	6.9
Dual-flush devices Sink-Bob	4	2.8	8.6
Econo-Flush	4	3.3	3.3
Flow-limiting shower head	11	4.6	1.0

67 percent for toilet flushing reuse and 50 percent for lawn watering reuse. These lower values may reflect natural apprehension for this more experimental part of the program. There is a need, however, for concern with home recycle from the aesthetics and particularly the public health standpoint. The responsibility for system operation and for ensuring adequate disinfection may rest with relatively untrained personnel, the homeowner or a building custodian, and for this reason, home recycle systems must be very reliable.

Estimates, based on cost of water saved, indicate that dual-flush modification of toilets and reduced-flow shower heads are cost effective. The shallow trap toilet should be considered for new installations or when malfunctioning toilets need replacing. Its relatively high initial and installation costs, however, do not justify its use for replacing workable toilets. Wash water recycle systems can be justified for homes in areas of relatively high water and sewerage charges, and also where recycle system installation could eliminate the need for modifying a septic tank system. These factors indicate that more experimental work on recycle systems for single homes is justified. Recycle systems for multiple dwellings should be even more attractive.

WSSC WATER CONSERVATION STUDY[5]

The Washington Suburban Sanitary Commission established a general program to promote water conservation during 1972. In conjunction with this program, tests were conducted in 2400 dwellings and 4800 flow-reducing devices were used.

The flow-reducing fixtures consisted of pressure-reducing valves, toilet inserts, and reduced-flow shower heads. The pressure-reducing valves reduced inlet pressures where supply pressures were excessive, and the toilet inserts, essentially, dammed off or displaced a portion of the flush-tank contents. A disadvantage of this displacement approach is that a full flush-tank volume is never available for flushing although an occasional second flush could be used if required. The volume displacement can be achieved by placing a brick in the flush tank; however, a safer and less expensive approach is inserting a water-filled, and weighted, used plastic bottle.

With the large number of dwellings involved in this study, maintenance was not consistent. The results for single-family homes where conditions were well controlled were very encouraging, however. Where toilet inserts were used in conjunction with pressure reduction to 50 psi (in most cases), water use was reduced by 30 percent and more. Reduced-flow shower heads lowered water use as much as 12 percent.

Most significantly, the study results were convincing enough to influence passing new plumbing codes, which require reduced-flow plumbing fixtures for new construction or remodeling. Also, WSSC has continued a user education program. The Commission is distributing water saving kits containing a booklet on water saving, dye tablets for tracing toilet tank leaks, and plastic bottles for inserting in toilet flush tanks to its customers in Montgomery and Prince George's Counties, Maryland.

SUMMARY AND PROJECTIONS

Completed studies indicate that there is justification for homeowners installing flow-reducing plumbing devices. Reduced-flow devices discussed in this paper are either on the market or have been developed through the prototype stage and could be mass produced easily. Reuse systems, however, are only at the pilot stage and need further development before being mass produced.

Because of the numerous factors involved, EPA proposes next to look at sociological, economic, and technical problems on a broader scale than that of individual homes. Total municipal use patterns may offer greater potential for water conservation. If careful consideration justifies further development of equipment for home water conservation, the next step would probably be to develop recycling systems for multiple dwelling use similar to that of the Electric Boat one. Large-scale demonstrations of water conservation and recycling would be proposed to obtain more statistically valid results. Other new concepts that appear attractive would be considered for demonstration and development to the stage where they are proven economically attractive and safe and have user acceptance.

In the meantime, the work discussed in this paper offers the homeowner incentive for water conservation. We hope that the work reported here will influence adoption of available equipment and techniques in the home in the immediate future.

ACKNOWLEDGMENT

Greatly appreciated are the efforts of contractors' and manufacturers' representatives and others interested in water conservation who contributed both directly and indirectly to the preparation of this paper. Special credit is due Sheldon Cohen and Harold Wallman of the Electric Boat Division of General Dynamics and Arthur P. Brigham of the Washington Suburban Sanitary Commission.

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FUTURE TOPICS

- *macroinvertebrate artificial substrate sampling,*
- *toxicological assessment of automotive catalytic emissions,*
- *fecal coliforms and fecal streptococci in sanitary landfills, and*
- *monitoring of organic removal unit processes for drinking water.*

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WATER SUPPLY RESEARCH

December 7, 1973

REMOVING ORGANIC MATTER FROM DRINKING WATER

Monitoring Treatment Processes

J. Keith Carswell, Ralph W. Buelow, and James M. Symons*

BACKGROUND

Organic matter that causes taste, odor, and toxicity is the major problem facing the waterworks industry today. During the 1969 Community Water Supply Survey (1) conducted by the organizational predecessor of the Water Supply Research Laboratory, the second most common complaint from consumers was that of bad taste and odor. The extent of the problem is also indicated by repeated recoveries of toxic organic chemicals from major rivers in the United States that serve as raw drinking water sources for many of our metropolitan areas.

Many water suppliers are attempting to provide taste and odor control through the use of powdered activated carbon. On the other hand, some 40 drinking water purveyors in the United States are attempting to control taste, odor, and organic content through the use of granular activated carbon, usually as a combination media for the filtration of particulates and the adsorption of organics. Unfortunately, these water purveyors have no reliable method of indicating the performance of the unit processes, except by the subjective determination of threshold odor number. Many suppliers have no knowledge of the organic content of their finished water. The objective of this study was to develop a technique that would permit any water purveyor to monitor the organic content of his finished water.

Organic measurement and identification is currently very sophisticated. The use of gas chromatography followed by mass spectrometry, with the unknown spectra compared with known spectra by computer, is currently permitting insight into the organic content of our waters that was never before possible. As exciting as this technique is, it is nevertheless a research tool that is far too expensive and complicated for water supply use. Even simple gas chromatography, or measurement of total organic carbon (TOC) (even if it were reliable in the 0-5 mg/l range), is too expensive for all but the largest water purveyors.

The technique chosen for this study was the adsorption of organic matter onto activated carbon followed by desorption with organic solvents. This method has three main advantages: (1) it has a long history in water supply use; (2) it is inexpensive to perform and simple enough to be performed by most analysts; and (3) it produces a final material that can be saved for reanalysis, should that be required.

The 1962 U.S. Public Health Service Drinking Water Standards contain a limit for carbon-chloroform extract (CCE) of 0.2 mg per liter. This limit was based on a technique developed by Middleton et al. (2) in the late 1950's called the carbon adsorption method (CAM). In spite of the usefulness of this test, it was not widely used in the waterworks industry. Our goal was to build on the background of this work and to improve the test.

PROJECT DESIGN

Sampling

A mini-sampler was designed for this study to be easily disassembled and packed into two small boxes for shipping or carrying. The mini-sampler is now commercially available through two companies, CFH Research Laboratories, Springfield, Massachusetts, and Belcan Corporation, Cincinnati, Ohio.* Plans and specifications are also available to anyone who wants to build a mini-sampler himself. The cost of materials is slightly over $200.

*The authors are with the Standards Attainment Branch of the Water Supply Research Laboratory, NERC-Cincinnati (513-684-8305); Mr. Carswell and Mr. Buelow are Research Sanitary Engineers and Dr. Symons is Chief of the Branch.

*Mention of commercial firms does not constitute an endorsement by the U.S. Environmental Protection Agency.

The quantity of adsorbant used in the mini-sampler was determined mainly by the capacity of the selected extraction apparatus. Robeck and Dostal, who started this project in 1962, reported (unpublished) that about 70 g of coal-based, granular activated carbon could be extracted in a 55/50 Soxhlet extraction apparatus using a 43- X 123-mm cellulose extraction thimble and that the use of this quantity of adsorbant would produce a measurable quantity of extract. The water to be sampled flows up through the sample column from a constant head tank providing a few centimeters of head at a flow rate of about 20 ml per minute. This gives a contact time between the water and carbon of approximately 4½ min. The sampling time is only 2 days, and the sample volume is about 60 liters, which is large enough to produce a measurable quantity of extract, but small enough to avoid any significant loss in activated carbon adsorption efficiency. Small changes in sample flow are not important because the total volume passing through the mini-sampler is measured using a sampling device developed by Castelli and Booth (3).

Extraction

Once the activated carbon has been exposed, it can be conveniently dried before extraction in small stainless-steel pans in an ordinary mechanical convection oven. The exposed activated carbon should be dried as rapidly as possible following the end of sampling to minimize any biodegradation of the adsorbed organics. Once dried, however, the activated carbon can be stored under refrigeration for an extended period of time before extraction without loss of significant organics.

The organics are desorbed in a Soxhlet extractor, which operates by cyclically exposing the activated carbon to freshly distilled solvents. Early in the development of the extraction procedure, a study was made to determine the influence of the total number of solvent cycles employed in the test on the final weight of the extract recovered. These studies showed that increasing quantities of extract can be obtained as the number of solvent cycles increases, up to approximately 400 solvent cycles. Beyond this point, a further increase in the total number of solvent cycles does not significantly increase the quantity of extract recovered. Therefore, extraction equipment was chosen that would provide sufficient heat to permit approximately 10 solvent cycles per hour, so that in about 2 days approximately 450 solvent cycles would be obtained for each solvent – chlororform and 95 percent ethyl alcohol. This maximizes the quantity of extract obtained and minimizes any analytical error that might develop if the total number of cycles obtained varied somewhat from experiment to experiment. Because less than 100 solvent cycles were used in the previous CAM technique, the increased number of solvent cycles used in this method partially accounts for the great increase in yield.

Because of the small solvent volumes used in the extraction test, extraction can be done on the bench in a well-ventilated laboratory; a special distillation hood, as was needed in the previous CAM technique, is not required. In addition, the small Soxhlet setup used with this method costs only about $45, but the large extractors needed with the previous CAM technique cost approximately $170. Finally, only about 6 man-hours are required to perform the extraction of a single sample, and this time is spread out over a 5-day period. Of course, more than 1 sample can be extracted at a time; in the authors' laboratory, 16 man-hours were required for the routine extraction of 6 samples per week by this method. This method is called the organics – carbon adsorbable (O-CA) procedure.

A color video-tape (also available as a 16-mm movie) entitled "The Determination of Organics in Drinking Water" shows how the O-CA test is performed; it may be borrowed at no cost from the Technical Information Office, NERC-Cincinnati. Running time is about 55 min. The O-CA has been proposed for inclusion in the 14th Edition of *Standard Methods for the Examination of Water and Wastewater*, to be published shortly.

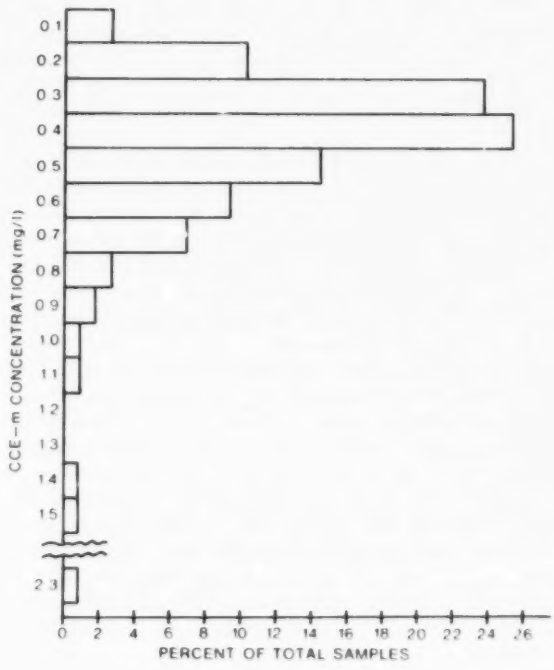

Figure 1. Frequency distribution of CCE-m concentration in finished water samples from 118 water supplies with surface sources.

Field Experience

To date, the O-CA procedure has been used by the U.S. Environmental Protection Agency (EPA) as part of its Interstate Carrier Water Supply Surveillance Program and in monitoring the performance of granular activated carbon beds at two water supplies. Several water purveyors have also purchased mini-samplers and are doing their own organic monitoring.

Interstate Carrier Water Supply Surveillance

The EPA has responsibility for determining the quality of drinking water in the approximately 725 water supplies around the country that provide water for interstate carriers (planes, trains, and buses). This surveillance is accomplished mainly through the 10 EPA regional offices. The water supply representative in each regional office has one or more mini-samplers of his own. These engineers take the mini-sampler out into the field, set it up at the water treatment plant of the water supply under investigation, expose the activated carbon, and then ship the exposed activated carbon to the Water Supply Research Laboratory's Surveillance Laboratory for extraction.

During the 12 months that the mini-sampler has been available, 118 different water supplies in 28 states, the District of Columbia, and Puerto Rico using surface water as a source have been sampled. The frequency distribution of these data are shown in Figures 1 and 2. Note, the lower case "m" indicates the mini-sampler was used to collect the samples. A comparison of these data with those obtained in 1962 indicates about a sixfold increase in CCE yield and about a thirteenfold increase in carbon alcohol extract (CAE) yield.

Data gathered by means of the mini-sampler were used by the technical committee responsible for rewriting a portion of the 1962 U.S. Public Health Service Drinking Water Standards. Based on these data, the proposal in the new EPA Drinking Water Standards is to have a limit of 0.7 mg per liter for CCE and 3.0 mg per liter for CAE as determined by this mini-sampler method.

Monitoring Granular Activated Carbon Beds

When the water supplies of both Lawrence, Massachusetts, and Davenport, Iowa, removed the sand from their old filter beds and replaced it with granular activated carbon (a media that should act both as a filtration media and an adsorption media), they proposed that the Water Supply Research Laboratory monitor the ability of these new activated carbon beds to remove organic matter as well as odor. Two conclusions were drawn from these studies: one, that odor was removed by granular activated carbon beds for a far longer period than organic matter, and two, that during certain periods, negative removal of CAE-type materials occurred.

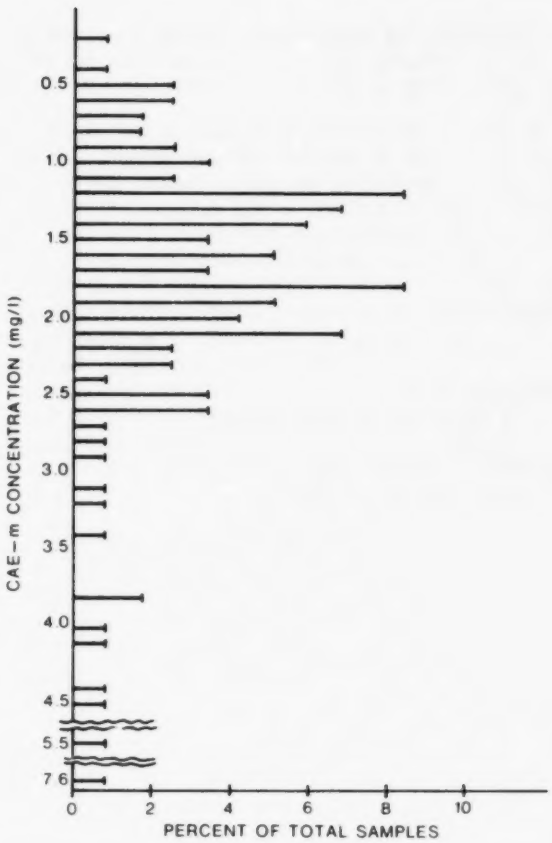

Figure 2. Frequency distribution of CAE-m concentration in finished water samples from 118 water supplies with surface sources.

CURRENT RESEARCH PROJECTS

The findings presented here have lead to the development of three in-house and two outside research projects conducted by Water Supply Research Laboratory personnel. Mr. J. Keith Carswell is investigating the use of oxidants as a supplementary or substitute method for removal of organic matter. Dr. O. Thomas Love, Jr., has an in-house project to determine: (1) the causes of negative removal of CAE-type materials that have occurred both at Lawrence and Davenport; (2) whether granular activated carbon can be used in a different manner to extend its life for organic removal; and (3) whether activated carbon exhausted for general organic matter removal can still remove specific toxic organics. In this regard, Dr. Love is also the project officer on a contract with the Lawrence Experiment Station, Massachusetts Department of Public Health, which is an

agency attempting similar studies, but with water that is more heavily laden with organic matter. They are also using fluorimetry as a monitor for organic removal.

Mr. Alan Stevens is attempting to determine whether other parameters of granular activated carbon, such as the phenol number and the iodine number, can be related to the performance of the activated carbon. In addition, he is working with both Carswell and Love in an attempt to show, by gas chromatographic analysis of the extracts from the O-CA monitoring of their treatment projects, which organics are removed during both oxidative and adsorptive treatment. In addition, Mr. Stevens is the project officer on a grant with Dr. Nancy Gerber (of Rutgers – The State University, New Jersey) who is producing the odorous compound geosmin. Mr. Stevens intends to use the purified geosmin as an identifiable odorous tracer that can be subject to various forms of organic removal treatment.

The results of these treatment research projects and continued field work should eventually provide the water supply industry with knowledge that will permit the design and operation of organic removal unit processes to ensure that consumers will be supplied with drinking water free of both odorous and toxic organic materials.

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ENVIRONMENTAL TOXICOLOGY RESEARCH

December 28, 1973

CATALYTIC CONVERTERS USED IN HEALTH EFFECTS STUDIES

J.K. Burkart, W. Moore, R.G. Hinners, and J.F. Stara*

BACKGROUND

The earth's atmosphere is a finite area that is continually contaminated by the introduction of various substances through the activities of man. The atmosphere has a limited capacity for self-cleansing, but in recent years, the explosive proliferation in the number and use of motor vehicles and their concentration in areas of high population density has resulted in atmospheric contamination from the exhaust emissions. In some areas, air pollutants have at times reached concentrations that are a threat to the health and well-being of the population. Such episodes have been well-publicized by the news media recently.

The increasing air pollution has been an area of concern for many years, as is evident by legislation designed to prevent and control it.[1] The Congressional Record states that the "growth in the amount and complexity of air pollution brought about by urbanization, industrial development, and the increasing use of motor vehicles, has resulted in mounting dangers to the public health and welfare, including injury to agricultural crops and livestock, damage to and the deterioration of property, and hazards to air and ground transportation. . . ." To control air pollution created by motor vehicles, legislation has provided for the establishment of motor vehicle emission standards (Clean Air Act, 1970), which require a 90-percent reduction in the emissions of carbon monoxide and hydrocarbons from light duty vehicles and engines manufactured during and after 1975. In 1976, nitrogen oxide emissions were scheduled to be reduced at least 90 percent below those of 1971 cars, but implementation of both standards has been extended 1 year. The national interim standards for 1975 that must be met for a car driven 50,000 miles are as follows: hydrocarbons (HC), 1.5 grams per mile; carbon monoxide (CO), 15.0 grams per mile; oxides of nitrogen (NO_x) 3.1 grams per mile.

*Messrs. Burkart and Hinners (Research Engineers) and Drs. Moore and Stara (Veterinarians and Toxicologists) are with the Environmental Toxicology Research Laboratory. Dr. Stara is Director of that Laboratory (513/684-7411).

STATE OF THE ART

The contribution of automobiles to atmospheric pollution has been recognized for some time, and efforts have been made to reduce pollution through additions to and modifications of the engine. Some of the changes that have been made include the PCV valve, manifold air injection, use of higher air to fuel ratios, and spark advance retard. However, it has become apparent that more drastic measures will have to be taken for automobiles to meet the Federal Emission Standards. Among the major approaches that have been considered are (1) development of alternate power systems and (2) development of control devices to reduce emissions from the engine (exhaust gas recirculation (EGR), catalysts, thermal reactors, fuel additives, and carburetor design changes). After careful consideration of the alternatives, the automobile industry has concluded that the optimal solution, at least for the present, consists of incorporating a catalytic converter in the exhaust train, optimizing the engine to obtain maximum efficiency from the converter, and making some changes in gasoline composition.

Catalytic Converters

The automotive and ancillary industries have developed and tested literally hundreds of catalytic converter prototypes. Generally speaking, the automotive catalytic converter is a device containing catalytic material capable of decreasing the concentration of emitted gases by increasing the rate of chemical reaction during their passage through the device. Currently, there are three basic catalytic systems under consideration:

(1) single-bed oxidation catalysts that remove HC and CO
(2) a dual-bed device having one oxidation catalyst bed to remove HC and CO and a separate reduction catalyst bed to remove NO_x
(3) a tricomponent or single-bed catalytic device that removes HC, CO, and NO_x simultaneously

The catalytic material in the converter may consist of noble metals (platinum and palladium), oxides of metals from the transitional group, or a combination of both deposited on a support structure made of alumina or silica. The noble metal catalysts seem to be the most efficient. Some of the specific structural and chemical formulations are considered "trade secrets."

Testing of the different types of devices has met with varying degrees of success. By far the greatest effort has gone into developing catalysts that oxidize HC and CO into carbon dioxide (CO_2) and water (H_2O). The HC/CO oxidation catalysts require excess oxygen (air) to convert HC and CO to H_2O and CO_2; this is accomplished by adding secondary air to the engine exhaust.

Efforts to develop a catalyst that will decompose NO in the presence of excess oxygen have been unsuccessful because the reaction rates are too slow. A number of catalysts promote the reduction of NO by the CO and hydrogen (H_2) present in an oxygen-deficient (reducing) atmosphere. This reaction is accomplished by operating the engine at a rich air-fuel mixture. Under these conditions and in the presence of a suitable catalyst, NO is converted, resulting in nitrogen (N_2), CO_2, and H_2.

Some of the catalysts used for the oxidation of HC and CO can also reduce NO if operated in the reducing conditions required for an NO_X catalyst. Since an NO_X catalyst requires a reducing atmosphere and the HC/CO catalyst requires an oxidizing atmosphere, if they are used together, they must be used in series in the exhaust system so that the exhaust conditions to each can be controlled. The two can be separated by some distance or be located within the same housing. The latter arrangement is commonly called a dual-bed catalyst and is favored by the warmup time required by HC/CO catalysts.

One of the major problems with NO_X catalysts has been the formation of ammonia (NH_3), which in itself is an objectionable exhaust product. Most of the NH_3 generated in the NO_X catalyst is re-oxidized in the HC/CO catalyst portion of the dual-bed reactor to NO_X and H_2O, thus defeating the purpose of the NO_X catalyst. A major effort in NO_X catalyst research has been to find one that not only has good NO_X conversion efficiency, but one that also produces minimum NH_3 and has satisfactory durability as well.

Theoretically, it should be possible to combine the functions of NO_X reduction and HC/CO oxidation in a single catalyst. At least one company has tested a tri-component catalytic converter with some success. However, the conversion efficiency is very sensitive to the air-fuel mixture, and a mechanism for sufficient control of the air-fuel mixture at the level required has not been developed.

Other Factors in Emission Control

The catalytic converter is only one component of the emission control systems being considered to meet the 1975-76 standards. The performance and life of the catalyst are dependent on engine operating conditions and other emission control components. In turn, the performance and characteristics of the catalytic converter affect the complete system.

Some of the major causes of catalyst degradation are: (1) lead coating, (2) thermal effects, (3) ignition failure, (4) vigorous vibration. In addition to lead–phosphorus, chlorine, bromine, and sulfur in the fuel are also detrimental. The HC/CO and NO_X catalysts have operating temperature limitations of approximately 1,400 F to 1,500 F for long-life durability. In the event of an engine malfunction, such as spark plug misfire, where large quantities of unreacted fuel can reach the catalysts, a thermal control system may be required to prevent damage to the converter.

Overtemperature protection for the catalytic converter is very important because of the need to (1) guard against converter burnup and vehicle fires and (2) preserve the emission control capability of the converter, since an excessive temperature excursion may cause catalyst destruction. In one approach, a temperature sensor triggers an air pump diverter valve that removes excess oxygen supply to the catalyst until it cools down. In view of the complexity and high cost of such overtemperature control systems, efforts are in progress to develop a catalyst with sufficiently high operating temperature capability.

The location of the catalytic converter relative to the exhaust manifold is also important. Because of the cold start requirements, it must be close enough to the manifold exhaust to warm up quickly, but be far enough removed to prevent overheating of the catalyst.

Some testing of motor vehicles using engines equipped with catalytic converters is currently in progress. The Ford Motor Company has a 450-car test fleet and General Motors has put more than 250 cars on the road to find out how well the pollution control devices work. Ford 1973 Galaxie 500 sedans are being used by the Federal General Services Administration, the State of California, and the McDonnel Douglas Corporation.

CURRENT RESEARCH

Engine and Exhaust Systems

The Environmental Toxicology Research Laboratory (ETRL) has acquired 1975 prototype engines equipped with catalytic converters for evaluation of possible health effects following exposure of animals to exhaust emissions. The engine systems under study are as follows:

Ford: 400 C.I.D., R-6 engine with R-14 calibration and the following controls:

(1) EGR
(2) air pump

(3) fluidic spark delay valve
(4) various temperature sensing triggers
(5) catalytic converter of monolith, noble metal oxidation type; two converters of this type are required – one for each bank of cylinders.

General Motors: 350 C.I.D. (engine shown in Figure 1)

(1) EGR
(2) air pump
(3) catalytic converter, pelletized type, noble metal oxidation catalyst; one converter after Y pipe.

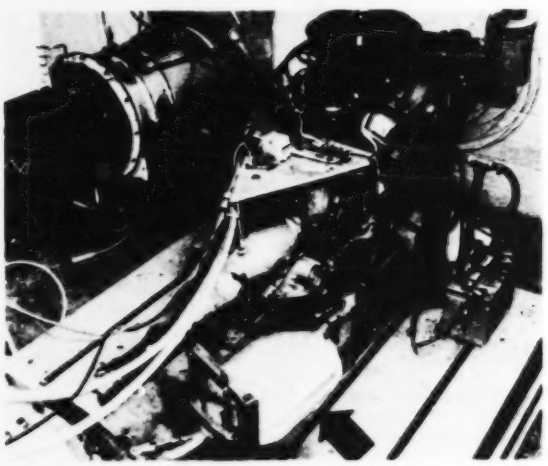

Figure 1. 1973 Chevrolet, 350 C.I.D. with pelletized catalytic converter (see arrow).

In addition to the engine and related equipment, the ETRL exposure system consists of a dilution tube, mixing chamber, distribution lines to the irradiation chambers (Figure 2), and animal exposure chambers (Figure 3). The whole exhaust must be diluted with air in a ratio of at least 10 to 1 to retain the particulate matter. For every pound of fuel burned, approximately 1 pound of water is formed and some condensation occurs if the exhaust is not immediately diluted with dry air. A portion of the exhaust/air mixture is then conducted to the irradiation chambers, where it is exposed to simulated sunlight for the production of photochemical smog. The facility is designed so that different groups of animals can be exposed to either control air, irradiated exhaust (simulated smog), or nonirradiated exhaust.

Table 1 illustrates how engine emission controls have changed the exhaust emission (irradiated exhaust) composition in exhaust studies conducted at this facility. The past emphasis has been on gaseous phase emission and ozone formation after dilution. Current investigation includes fuel additives and control devices with emphasis on particulates and trace elements.

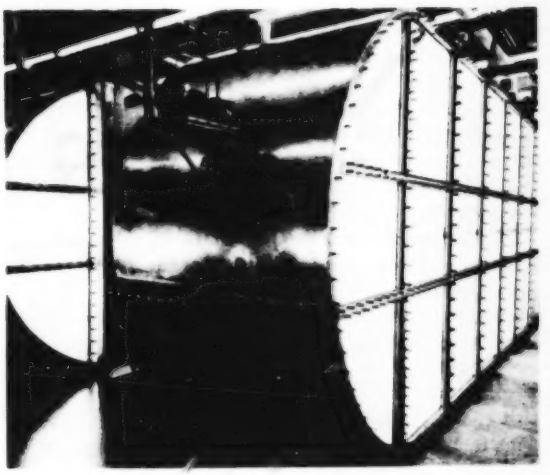

Figure 2. Irradiation chambers.

TABLE 1. EXHAUST EMISSION (IRRADIATED EXHAUST) FROM 1961-1975 MODEL ENGINES

Engine model year	Tailpipe CO (ppm)	HC/NO* ratio	Oxidant formed
1961	50,000+	15/1	Yes
1965-67	30,000	12/1	Yes
1972	2,000	4/1	(No O_3; some NO_2 conversion)
1975	60	1/8	Trace

*Approximate minimum HC/NO_x of 6/1 for ozone formation.

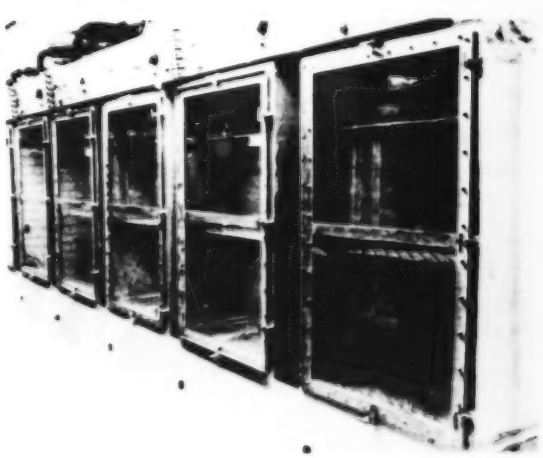

Figure 3. Animal exposure chambers.

Animal Studies

As part of the Environmental Protection Agency's effort to reduce automotive pollution, ETRL is studying the toxic effects of whole emissions as well as the effects of single pollutants, either existing or to be introduced into the environment by mobile and stationary sources. The pollutant may be emitted from fuel, oil, an additive, an engine, or an emission control device.

The toxicologic investigations at ETRL are conducted in series of acute, subacute, and chronic studies. In the acute studies, animals are usually exposed for 1 week to the whole emissions, using relatively high concentrations to produce biological effects. An example of such a study would be the comparison of the effects in animals of exposure to exhausts from the automotive system with and without the catalyst. A single pollutant experiment is, for example, the inhalation of palladium to determine pathological effects in the lungs and other organs of interest.

The subacute studies are designed to determine specific biological effects on the whole organism and on sensitive organs and/or tissue systems, using lower, more realistic exposure levels. These studies have a duration of a month or longer, and they comprise the major portion of the ETRL automotive emission program. A 2-month study has just been completed in which animals were exposed to the exhaust from fuel containing an organic manganese additive used as an antiknock agent. Another example is the study of cardiovascular effects in primates ingesting cadmium.

The chronic studies represent only a small portion of the ETRL research effort because of their duration and cost. The parameters measured are carefully selected on the basis of acute and subacute data in order to obtain maximum results from minimum manpower effort and funds. Previous studies have been conducted with animals chronically exposed to inhalation of irradiated auto exhaust.[2] Also, a 7-year chronic study using relevant urban levels of auto exhaust, simulated smog, and other air pollutants is nearing completion.[3]

To comply with emission standards, the automotive industry continuously introduces new fuels, additives, and control devices. ETRL provides the background health intelligence – specifically, toxicologic effects data required as a guide in making regulatory decisions concerning pollution of the environment from mobile and stationary sources and in various environmental media. The current research provides necessary information that is largely unavailable from any other source.

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